# ATTACHMENT F

# ESTIMATION OF EXPOSURE OF PERSONS TO METHYL BROMIDE

# ESTIMATION OF EXPOSURE OF PERSONS TO METHYL BROMIDE DURING AND/OR AFTER AGRICULTURAL AND NONAGRICULTURAL USES

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#### **EXECUTIVE SUMMARY**

Methyl bromide (MB) has been used extensively to fumigate soil, agricultural commodities and structures in California. Total reported use of MB from 1996 to 1999 was 16.0, 15.7, 13.6 and 15.3 million pounds, respectively. In 1999, strawberry, soil application (preplant-outdoor) and outdoor container/field grown plants accounted for 55% of the total annual use.

This exposure document was prepared as part of the Department of Pesticide Regulation's risk assessment process. The document contains information, including physical/chemical properties, regulatory history, formulations, usage, label precautions, human illnesses, dermal toxicity and sensitization, animal/human metabolism, inhalation uptake/dermal absorption, and exposure assessment. MB exposure estimates for workers and other persons were calculated, if applicable, using air concentrations of MB, duration and frequency of exposures. Exposure estimates are shown as the 24-hour Time-Weighted Average (TWA) unless indicated otherwise.

Due to its high vapor pressure, the major route of exposure is by inhalation. Major excretion routes in rats after inhalation exposure occurred in exhaled air and urine. From 1991 to 1999, illnesses in California caused by MB alone were 90 cases (average 10.0 cases/year) and those caused by MB in combination with chloropicrin were 106 cases (average 11.7 cases/year). From 1982 to 1999, there were six accidental exposures where 253 people were evacuated. From the same period, there were 19 deaths resulting entirely from structural fumigation.

Exposure assessments for MB were determined for occupational workers and other persons, including residents of nearby homes. Examples of average (or range of average) acute exposure estimates (part per billion, ppb) calculated as the 24-hour TWA are:

- preplant soil injection fumigation, 0.6 835,
- soil fumigation in greenhouses, 0.009 (tarpaulin (tarp) venters) and 0.95 (tarp removers),
- fumigation of grain products, 0.03 16.0,
- dried fruit and tree nut fumigation, 4 1,434,
- a walnut processing facility, 29 239,
- a brewery facility, 25 173.

The 95<sup>th</sup> percentile acute MB exposures of persons at the buffer zone distance range from 163 to 239 ppb, depending on field sizes (1 to 10 acres) and soil application methods (such as nontarp/shallow/bed, tarp/deep/broadcast, tarp/shallow/broadcast). For example, the MB air concentration for a 10-acre field when nontarp/shallow/bed fumigation method was used was 217 ppb and that when tarp/shallow/broadcast fumigation method was used was 165 ppb. The maximum ambient MB concentrations (ppb) in the high use counties (Monterey, Santa Cruz and Kern) were 30.8 (daily), 15.5 (weekly), and 7.68 (mean of weekly means). The meaning of ambient MB concentrations are: 1) maximum daily MB concentration represents the highest observed 24-hour MB concentrations in one of the sampling stations; 2) maximum weekly mean represents the highest observed weekly average in one of the sampling stations; 3) maximum mean of weekly means represents the highest observed weekly average in one of the sampling stations. The sampling period lasted 7 or 8 weeks.

Several applications of MB such as soil fumigation in nurseries and greenhouses, fumigation of homes and fumigation of noncertified chambers, which were used in exposure monitoring studies, were not conducted in accordance with permit conditions/regulations. Thus, exposure data from these studies are not included in this document because the influence of factors required by permit conditions/regulations to MB concentrations is not known. These studies were performed during fumigation of potting soil, greenhouse (except tarp venters and removers), grain products (except aerators and forklift drivers), dried fruits and tree nuts (except chamber-raisins), cherries, walnut processing facility (except fumigation in 1994), residents/bystanders in fumigated homes and reentry studies for fumigated homes.

Some MB exposure data are grouped based on types of fumigation and exposure scenarios. The purpose of grouping of exposure data is to show the magnitude of the exposure data and whether mitigation measures would cover a wide range of exposure. Examples of the average (range) of acute MB concentrations (ppb) for soil fumigation are 136 (3 - 515) for nonbedded, 93 (1 - 334) for bedded), and 123 (1 - 518) for bedded and nonbedded, and 83 (1 - 404) for commodity fumigation (other workers).

Acute and nonacute MB exposures (7-day, 90-day, and 365-day exposure periods) of persons during soil, commodity, and structural (brewery facility) fumigations were recalculated using work hours allowed by the current soil fumigation regulations or permit conditions, instead of using work hours from a survey. Examples of the ranges of the adjusted average exposures during field fumigations are: 0.4 - 974 ppb for acute exposure, 0.2 - 696 ppb for subacute exposure (7-day exposure period), and 1.0 - 595 ppb for subchronic exposure (90-day exposure period). Upper bound MB concentrations for acute exposures were also calculated. The upper bound acute exposures range from 1 to 2,118 ppb for soil fumigation. The maximum MB exposure of persons during greenhouse, commodity, and structure (brewery facility) fumigations was assumed to be 210 ppb because MB concentrations in work areas must be monitored and work hours be adjusted accordingly so that the daily MB exposure is not greater than 210 ppb, which is the target exposure level.

The Department of Pesticide Regulation does not have data to assess all worker exposure scenarios or potential exposure to the public from all MB applications. Nonacute exposures were also estimated for different work tasks and exposure scenarios. These exposures were estimated from acute exposure, duration and frequency of exposure for each specific exposure scenario. Ambient air concentrations were shown as daily (maximum 24-hour and 95<sup>th</sup> percentile), weekly (maximum and 95<sup>th</sup> percentile weekly mean) and mean of weekly means (7- or 8-week).

Adverse effects of MB, which were used to establish the endpoints for the critical no-observed-effect levels for risk assessment, were developmental toxicity (acute), neurotoxicity (subchronic), and nasal epithelial hyperplasia and degeneration (chronic).

# TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	. 2
TABLE OF CONTENTS	4
ROAD MAPS FOR APPENDICES, TABLES AND CALCULATIONS	7
a) A road map for appendices and tables of the MB exposure document	
b) A road map for calculations of subacute, subchronic and chronic exposures of MB	
INTRODUCTION	
PHYSICAL AND CHEMICAL PROPERTIES	10
REGULATORY HISTORY INCLUDING U.S. EPA STATUS	
FORMULATIONS	
USAGE	
LABEL PRECAUTIONS/PERSONAL PROTECTIVE EQUIPMENT	
HUMAN ILLNESSES	16
DERMAL TOXICITY AND SENSITIZATION	
ANIMAL/HUMAN METABOLISM	20
INHALATION UPTAKE/DERMAL ABSORPTION	21
Inhalation uptake	21
Dermal absorption	21
FARM COMMODITY RESIDUES	23
EXPOSURE ASSESSMENT	
Exposure calculation procedures	
a) Acute exposures	
b) Nonacute exposures	
Definitions.	
Availability of worker exposure studies	
a) Summary of MB exposure studies conducted before 1992	
b) Summary of MB exposure studies conducted in and after 1992	21
EXPOSURE APPRAISALS	31 37
ACKNOWLEDGMENT	
REFERENCES	39
Appendix A Duration and Frequency of Acute and Nonacute Exposures for Workers	40
and Residents	
Appendix B Worker Exposure Studies	54
Methyl bromide studies conducted in and after 1992.	54
1. Preplant soil injection fumigation (including aeration, tarp removal)	54
a) Shallow-shank tarp method for MB fumigation: Worker exposure	54
b) Nontarp deep injection for measurement of MB exposure to the applicator,	
applicator assistant and cultipacker tractor driver	58
c) Exposure of workers to MB during a deep shank, nontarp soil fumigation near	
Traver, Hanford and Madera in California	60
d) Deep shank, nontarp soil fumigation: Mitigation of MB exposure	
(near Helm, California)	61
(near Helm, California)e) Shallow shank, tarped-bed soil fumigation: Worker exposure	62
f) Tarped-bed fumigation: Mitigation of MB worker exposure	64
g) Tarped-bed fumigation for measurement of MB exposure to the applicator,	
applicator assistant, and shovelman	65
h) MB exposure to the tarpaulin cutter and remover positions from tarped-	
shallow broadcast fumigation	67
i) Worker exposure to MB during tarp cutting and removal	60
1) "TOTACL CAPOSITE to THE Guilling time cutting and removal	

2. Soil f	fumigation in nurseries and greenhouses	71
a)	Worker exposure assessment during potting soil fumigation	71
b)	Exposure of workers to MB during soil fumigation in greenhouses	71
3. MB r	nonitoring: The Grain Product Group	73
4. Detei	rmination of MB exposure during dried fruit and tree nut fumigation practice	75
5. MB:	Measurement of exposure to fumigators, forklift drivers, cherry sorters	
	other workers	79
6. Work	ker exposure and on-site air monitoring studies at a walnut processing facility	. 79
	e-type fumigation: Potential worker exposure to MB at a brewery facility	
	ping of acute MB exposure estimates of handlers during soil fumigation	
	Air concentrations obtained from nonbedded and bedded fumigation	
b)	Air concentrations obtained from nonbedded soil fumigation	.84
	Air concentrations obtained from bedded soil fumigation	.85
d)	Air concentrations obtained from commodity, greenhouse and	
	space-type fumigations	85
Appendix (	C Residential Exposure Studies	87
	lential Exposure Studies	87
a)	Residents/bystanders (outdoor and indoor air concentrations of MB near	
	fumigated single-family houses	87
b)	Residents/bystanders (downwind outdoor and indoor air concentrations	
	of MB during aeration of fumigated single-family houses	87
2. Expo	sure of residents to MB during reentry into fumigated houses	87
	sure of residents to MB from living near commodity fumigation facility	
	sure of residents to MB from living at the buffer zone distance	
	D Exposure of Persons to Ambient Methyl Bromide in the High Use Counties	
1. Amb	ient MB monitoring study in Monterey and Santa Cruz Counties	95
2. Amb	ient MB monitoring study in Kern County	95
	ulations of MB air concentrations	
	E Adjusted Acute and Nonacute Exposure Estimates of Persons in California	
rippelial x 1	to Methyl Bromide	ΛC
	to Methyl Bronniae	90
LIST OF T.	ARIFS	
Table 1.	Methyl bromide products registered in California in 2001	13
Table 2.	Summary of methyl bromide usage in 1996 from the DPR database:	. 1.
1 4010 2.	Top ten uses	14
Table 3.	Summary of methyl bromide usage in 1997 from the DPR database:	1
Tuoic 5.	Top ten uses	15
Table 4.	Summary of methyl bromide usage in 1998 from the DPR database:	1.
14610 11	Top ten uses	15
Table 5.	Summary of methyl bromide usage in 1999 from the DPR database:	10
24610 61	Top ten uses	15
Table 6.	Occupational and nonoccupational illnesses associated with exposure to	10
24610 01	methyl bromide alone in California (1991-1999)	17
Table 7.	Occupational and nonoccupational illnesses associated with exposure to meth	vl
	bromide in combination with other pesticides in California (1991-1999)	
Table 8.	Symptoms described by patients exposed to methyl bromide alone	
	and in combination with chloropicrin in California (1991-1999)	19
Table 9.	A log-linear regression analysis of residue data over time from methyl	_
	bromide chamber fumigation of various commodities	. 25
Table 10.	Air concentrations of methyl bromide near the worker's breathing zone	30
Table 11.	Summary: Acute and nonacute exposure estimates of persons in California	

T. 1.1. 10		32
Table 12.	Summary: Acute methyl bromide exposure (95 <sup>th</sup> percentile) of persons at the	25
	buffer zone distance following field fumigation	35
Table 13.	Summary: Grouping of methyl bromide acute exposure estimates for workers	
Table 13.		36
Table 14.	Methyl bromide concentrations (ppb) based on the Air Resources Board 2000	50
Tuble 11.		36
Table B.1.	Exposure of applicators to methyl bromide (MB) during shallow shank-	
	tarped soil injection fumigation	56
Table B.2.	Exposure of co-pilots to methyl bromide (MB) during shallow shank-tarped	
	soil injection fumigation	57
Table B.3.	Exposure of shovelmen to methyl bromide (MB) during shallow shank-tarped	
		57
Table B.4.	Exposure of tarpaulin removers employed by pest control operators to	
	methyl bromide (MB) during collection of tarp from shallow shank-tarped	
m 11 D #		58
Table B.5.	Exposure of tarpaulin removers employed by growers to methyl bromide (MB	
T 11 D 6	during collection of tarp from shallow shank-tarped soil injection fumigation	.58
Table B.6.	Exposure of applicators, applicator assistants and cultipacker tractor	50
Table D 7	$\mathcal{J}$	59
Table B.7.	Methyl bromide (MB) air concentrations near the workers' breathing zone	
	and the estimation of worker exposure (nontarp soil fumigation near Traver, Hanford and Madera in California)	61
Table B.8.	Methyl bromide (MB) air concentrations near the workers' breathing zone	01
Table D.o.	and the estimation of worker exposure (deep shank nontarp soil fumigation	
		62
Table B.9.	Exposure of workers to methyl bromide (MB) fumigation using conventional	02
Tueste Biss.		63
Table B.10.	Exposure of workers to methyl bromide (MB) during application using	-
	exposure mitigation method	65
Table B.11.	Exposure of handlers to methyl bromide (MB) during shallow shank,	
		67
		69
Table B.13.	Exposure of tarp cutters and removers to methyl bromide (MB) following	
m 11 D 14		71
Table B.14.	Exposure of tarp venters and removers to methyl bromide (MB) during	70
T-1-1- D 15	soil fumigation in greenhouses	13
Table B.15.	Exposure of workers to methyl bromide (MB) during and after fumigation of grain products	75
Table B 16	Exposure of workers to methyl bromide (MB) during and after fumigation of	13
Table D.10.	dried fruit and tree nut products	78
Table B 17	Methyl bromide (MB) air concentrations obtained from worker exposure	70
1 aoic <b>D</b> .17.	studies, and area and on-site air monitoring studies at a walnut processing	
	plant in stockton	81
Table B.18.	Monitoring of methyl bromide (MB) during space fumigation and aeration	01
10010 20100	at a brewery facility	83
Table B.19.		
	during fumigations of soil, commodity and brewery facility	86
Table C.1.	Exposure of residents to airborne methyl bromide during commodity	
	fumigation	89
Table C.2.	fumigation	
	based on different emission rates and field sizes	90
Table C.3.	Emission rates for different application methods when using maximum	

	applied rates	95
Table C.4.	Acute methyl bromide (MB) exposures (95 <sup>th</sup> percentile) of persons at the	
	buffer zone distance following field fumigation	94
Table D.1.	Methyl bromide concentrations (ppb) based on Air Resources Board	
	2000 monitoring studies in Monterey, Santa Cruz and Kern Counties	97
LIST OF F	GURES	
Figure 1.	A Road map for Appendices and Tables of the Methyl Bromide Exposure	
	Document	8
Figure 2.	A Road map for Calculations of Subacute, Subchronic and Chronic	
	Exposures of Methyl	9

02

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# ROAD MAPS FOR APPENDICES, TABLES AND CALCULATIONS

The National Research Council peer reviewed the exposure document for MB and recommended that a road map of the information in the appendices and a more systematic presentation of the data would be helpful to the reader. Two road maps are provided for this purpose in the form of flow diagrams as follows:

a) A road map for appendices and tables of the MB exposure document: This flow diagram indicates appendices and tables contained in this exposure document. The authors also provide a brief description of contents in these appendices and tables. However, a road map within an appendix is deemed unnecessary because each appendix is self-explanatory in nature.

This flow diagram also shows the arrangement of tables. Basically, these tables are arranged according to the document format for sections. Summary tables (Tables 11 to 14) for exposure data are located ahead of other tables that contain exposure data from individual study because of the recommendation from the reviewers.

b) A road map for calculations of subacute, subchronic and chronic exposures of MB: This road map provides a quick glance for exposure calculations. Basically, the exposure data are adjusted to reflect the recovery and maximum application rate allowed by product labels. The magnitude of exposures for acute, subacute, subchronic and chronic exposures are also dependent on duration and frequency of exposure. Duration and frequency of exposure were obtained from surveys as well as from default values, if data were not available. These data are shown in Appendix A. Stepwise calculations are shown in the flow diagram.

Figure 1. A Road Map for Appendices and Tables of the Methyl Bromide Exposure Document

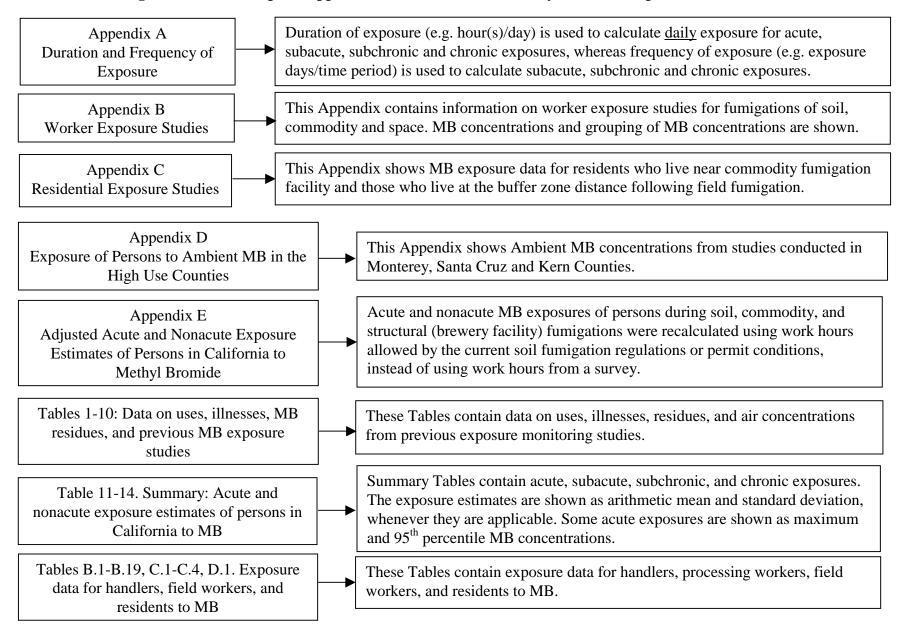
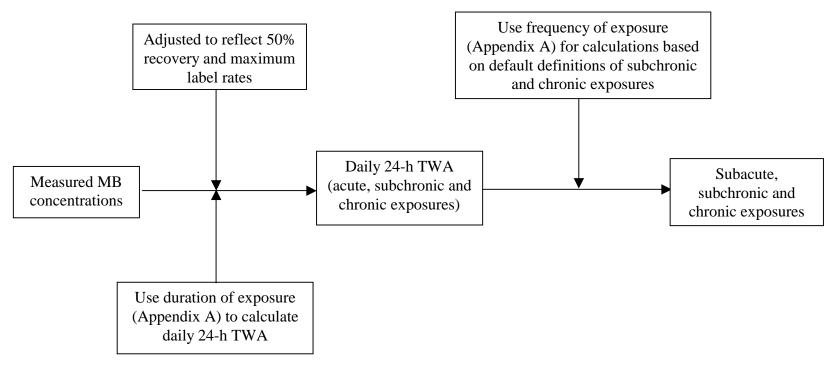


Figure 2. A Road Map for Calculations of Subacute, Subchronic and Chronic Exposures of Methyl Bromide



Example of subchronic exposure calculation:

Measured MB Concentration (ppb)	· , , , , , , , , , , , , , , , , , , ,		Duration of exposure 5 hours/day	Frequency of exposure (exposure days/90-day period)
397	400/280	50	5/24	55/90
Daily subchronic expos	ure (24-h TWA): 397 x 400 x 1	$\frac{00 \times 5}{50  24} = 236$	ppb	
Subchronic exposure:	236 x 55 90	= 144	ppb	

# Department of Pesticide Regulation Worker Health and Safety Branch

**Human Exposure Assessment** 

HS-1659 February 5, 2002

#### INTRODUCTION

Methyl bromide is widely used as a fumigant to control pests in soil, fresh and dry agricultural products, residences and other structures. This fumigant is acutely toxic to humans from excessive inhalation exposure. In order to reduce potentially harmful exposures to users and residents/bystanders, the Department of Pesticide Regulation (DPR) issued permit conditions for soil injection fumigation, soil fumigation within the greenhouse, fumigation of tarped potting soil, and commodity fumigation. Recently, DPR adopted regulations pertaining to the use of methyl bromide in structural fumigations and the use of methyl bromide in soil fumigations prior to the planting of agricultural crops. Currently, DPR is working on the risk assessment of MB under the provision of the Birth Defects Prevention Act of 1984. The Worker Health and Safety Branch (WH&S) is responsible for the preparation of the MB exposure assessment document, which is an integral part of the risk assessment process.

Many exposure monitoring studies were conducted prior to the implementation of permit conditions/regulations and may not reflect exposure after restrictions were implemented; these studies were soil fumigation, nursery potting soil fumigation, greenhouse soil fumigation, fumigation of grain products, fumigation of dried fruit and tree nut products, fumigation at a walnut processing and a brewery facility, and fumigation of houses. DPR does not have data to assess all worker exposure scenarios or potential exposure to the public from all MB applications.

The exposure assessment document contains sections dealing with physical and chemical properties, regulatory history, formulations, usage, label precautions, human illnesses, dermal toxicity/sensitization, animal/human metabolism, inhalation uptake and dermal absorption. Information from these sections enhances better understanding of the nature, usage, and potential for exposure. Exposure estimates are presented as the 24-hour time-weighted-average (TWA) air concentration of MB. These estimates are grouped as acute exposure (daily exposure) and nonacute exposures (subacute, subchronic, and chronic exposures).

The Subcommittee on Methyl Bromide of the National Research Council reviewed the 1999 MB risk characterization document, which included the exposure document (October 5, 1999). The Subcommittee provided comments and recommendations in the report (NRC, 2000). This revision of the exposure document incorporates comments from the Subcommittee when they warrant changes.

On December 3, 2001, the exposure for applicators and co-pilots during shallow shank, tarped-bed fumigation (Table 11, g) was changed to reflect correct methyl bromide concentrations. The exposure for irrigation pipe tractor drivers and pipelayers were deleted because these work tasks are not allowed during MB soil fumigation until the restricted entry interval has expired.

# PHYSICAL AND CHEMICAL PROPERTIES

Physical and chemical properties of MB as mentioned below were obtained from the Farm Chemicals Handbook (Meister, 1995), the Merck Index (Budavari *et al.*, 1989), and United States Environmental Protection Agency (U.S. EPA, 1986a).

Chemical name: Bromomethane, monobromomethane

CAS Registry number: 74-83-9 Common name: Methyl bromide

Trade names: Brom, Brom-O-Gas, M-B-R, Metabrom, Meth-O-Gas, Methyl Bromide, Pic-Brom,

Terr-O-Gas, Tri-Brom, Tri-Con, Tri-Pan.

Molecular formula: CH<sub>3</sub>Br Molecular weight: 94.95 g/mole Chemical structure: CH<sub>3</sub>-Br

Physical appearance: Colorless gas, usually odorless; sweetish, chloroform-like odor at high

concentrations (odor threshold at 80 mg/m<sup>3</sup> or 20.6 ppm); burning taste. It is

nonflammable in air but does burn in oxygen.

Solubility: 1.75 g/100 g water (20 °C, 748 mm Hg), forms a crystal hydrate, CH<sub>3</sub>Br.20H<sub>2</sub>O, below 4

°C; freely soluble in alcohol, chloroform, ether, carbon disulfide, carbon tetrachloride,

benzene.

Boiling point: 3.56 °C Melting point: -93.66 °C

Octanol/Water partition coefficient: Log P = 1.19 (15.5:1) Vapor pressure: 1420 mm Hg (20 °C), 2600 mm Hg (40 °C)

Specific gravity: 1.7 g/mL (liquid) Vapor density: 3.3 g/L (gas)

Conversion factor: 1 ppm =  $3.89 \text{ mg/m}^3$  at  $25 \,^{\circ}\text{C}$ 

# REGULATORY HISTORY INCLUDING U.S. EPA STATUS

The insecticidal activity of MB was first reported in 1932 (Le Goupil, 1932). MB is a restricted use pesticide in the United States. Retail sale and use are limited to certified applicators or persons under their direct supervision, and only for those uses covered by the applicator's certification.

# Ozone depletion:

- 1. MB is an ozone depleter with a calculated ozone depletion potential (ODP) of 0.7 (Watson *et al.*, 1992).
- 2. The worldwide sources of MB include: Anthropogenic (human made) agriculture, biomass burning (forest fires, grass fires), leaded gasoline burning, and oceans.
- 3. U.S. Clean Air Act mandated that by the year of 2005, no production or importation of MB is allowed. However, the Act does not restrict the use, which is regulated under the Federal Insecticide, Fungicide and Rodenticide Act in the U.S. EPA, Office of Pesticide Programs.
- 4. At the 1997 meeting, Parties (over 125 nations) to the Montreal Protocol amended the previous deadlines. The new deadlines on complete phase-out of use are 2015 and 2005 for developing and industrial nations, respectively.

# Federal Regulations:

1. The U.S. EPA established tolerances in commodities based on inorganic bromide level because of the assumption that MB is degraded completely to bromide (Federal Register, 1991).

- 2. The oral reference dose (RfD) was determined to be 0.0014 mg/kg/day based on the no-observed-effect level (NOEL) of 1.4 mg/kg/day for forestomach epithelial hyperplasia in a rat oral subchronic study (Danse *et al.*, 1984) and an uncertainty factor of 1,000. The inhalation reference concentration (RfC) was 5 x 10<sup>-3</sup> mg/m<sup>3</sup> (1.3 parts per billion, ppb) based on the lowest-observed-adverse-effect level (LOAEL) of 3 ppm for nasal olfactory epithelial hyperplasia from a rat chronic inhalation study (Reuzel *et al.*, 1987 and 1991) and an uncertainty factor of 100.
- 3. The drinking water health advisories for MB for one-day, ten-day, and longer-term health advisory for a child is 0.1 mg/L assuming 1 L/day water consumption for a 10-kg child (U.S. EPA, 1992). The longer-term health advisory for an adult is 0.5 mg/L assuming 2 L/day water consumption for a 70-kg adult. The lifetime health advisory is 0.01 mg/L assuming 20% of exposure by drinking water.
- 4. MB is classified as a "Group D" carcinogen (not classifiable as to human carcinogenicity) by U.S. EPA due to inadequate human and animal data (U.S. EPA, 1992).

# California Regulations:

- 1. For occupational exposure to MB, the current permissible exposure limit (PEL) for MB is 5 ppm or 20 mg/m<sup>3</sup> and a ceiling limit of 50 ppm.
- 2. In 1992, monitoring data caused the DPR to be concerned regarding the risk from short-term exposures to MB both to structural workers and residents returning to recently fumigated structures. The DPR promulgated emergency regulations to decrease the exposure and required pest control operators to hand out a Fact Sheet explaining the potential human hazards of MB fumigation. Permit conditions were developed for soil, and commodity fumigation.
- 3. On January 1, 1993, MB, as structural fumigant, was administratively listed by the Office of Environmental Health Hazard Assessment (OEHHA) as a developmental toxicant under Proposition 65 via the provision for listing due to the federal label warning requirement.
- 4. The Proposition 65 Developmental and Reproductive Toxicity Identification (DART) Committee of the OEHHA Science Advisory Board decided that evidence from experimental animals had not "clearly shown" that MB caused developmental and reproductive toxicity. MB remains listed under Proposition 65 for structural fumigation uses only.
- 5. The regulation for the use of methyl bromide in structural fumigations was approved on August 15, 2000 and effective on September 14, 2000.
- 6. The regulation for the use of methyl bromide in soil fumigations prior to the planting of agricultural crops was approved on December 15, 2000 and effective on January 14, 2001.

#### **FORMULATIONS**

In 2001, 54 MB-containing products were registered in California. Table 1 shows % active ingredient (a.i.) and trade (product) names of these products. Some products contain chloropicrin as a warning agent. Chloropicrin is also a fumigant similar to MB in controlling pests. Detailed information on application rate and sites is available from the DPR home page. There is too much information to summarize or provide as hard copy in this document. Table 1 presents a DPR database search of MB active products as of April 26, 2001.

Table 1. Methyl bromide products registered in California in 2001.

, ,				% Chloropicrin
Product Name	Formulation	Company	% MB	listed as a.i.
50-50	P	A	50	50
57-43	P	A	58	43
67-33	P	G	67	33
67-33 Preplant Soil Fumigant	P	A	67	33
75-25	P	A	75	25
80-20	PG	A	79	19
98-2	P	G	98	0
98-2 Contains 2% Chloropicrin	P	A	97.6	0
Brom-76	PG	S	75	1
Bromo-O-Gas (Liquid)	PG	G	98	0
Bromo-O-Gas 0.5%	PG	G	99.5	0
Bromo-O-Gas 0.25%	P	G	99.75	0
Bromo-O-Gas 2%	P	G	98	0
MBC-33 Soil Fumigant	P	T	67	33
MBC Concentrate Soil Fumigant	P	T	98	0
M-B-R 98	P	AL	98	0
M-B-R 98 Technical	P	AL	98	0
Metabrom 100	P	A	99.7	0
Metabrom 99	P	A	99.65	0.25
Metabrom Q	PG	A	100	0
Meth-O-Gas 100	PG	G	100	0
Meth-O-Gas Q	P	G	100	0
Methyl Bromide	P	G	100	0
Methyl Bromide 100	PG	S	100	0
Methyl Bromide 100	PG	A	100	0
Methyl Bromide 89.5%	PG	T	89.5	0
Methyl Bromide 98%	P	S	98	0
Methyl Bromide 98%	PG	T	98	0
Methyl Bromide 99.5%	PG	G	99.5	0
Methyl Bromide 99.5%	PG	S	99.5	0
Methyl Bromide 99.5%	PG	T	99.5	0.5
Methyl Bromide 99.75%	PG	S	99.75	0
Methyl Bromide Quarantine Fumigant	PG	S	100	0
Pic-Brom 25	PG	S	75	25
Pic-Brom 33	PG	S	67	33
Pic-Brom 43	PG	S	57	43
Pic-Brom 50	PG	S	50	50
Pic-Brom 55	PG	S	45	55
Pic-Brom 67	PG	S	33	67
Terr-O-Gas 57	PG	G	57	41.5
Terr-O-Gas 67	PG	G	67	33
Terr-O-Gas 75	PG	G	75	25

Table 1 (cont.). MB products registered in California in 2001.

% Chloropicrin listed as a.i. **Product Name** Formulation Company % MB PG Terr-O-Gas 80 G 80 20 Terr-O-Gas 98 P G 98 2 P T 99 Tri-Brom 0 Tri-Con 45/55 P T 45 55 PG T Tri-Con 50/50 50 50 PG T 57 Tri-Con 57/43 42.6 Tri-Con 67/33 PG T 67 32.7 T Tri-Con 75/25 PG 75 24.8 P Tri-Con 80/20 T 80 19.8 P Tri-Con 80/20 SM 80 19.8 Tri-Pan 76/24 PG T 75 24.0 TriCal Methyl Bromide 99.5% P SM 99.5 0

P = pressurized liquid/sprays/foggers; PG = pressurized gas; A = Ameribrom, G = Great Lakes, S = Soil Chemical Corp; AL = Albermarle; T = TriCal; SM = Shadow Mountain (part of TriCal)

# **USAGE**

The annual top-ten uses of MB (DPR, 1999a, 1999b, 2000a, 2000b) are shown in Tables 2-5. The highest percentages of MB use in those years were for strawberry planting, ranging from 26% to 34% of the total annual reported use. The percentages of annual top-ten uses from 1996-1999 calculated based on the total annual reported use were 72%, 76%, 74%, and 76%, respectively.

Table 2. Summary of methyl bromide usage in 1996 from the DPR database: Top ten uses.

Usage	Lbs methyl bromide	% Total
Strawberry (All or Unspecified)	4,375,225	27
Grapes, wine	1,479,859	9
Soil application, preplant-outdoor (seedbeds, etc.)	1,407,539	9
Outdoor container/field grown plants	1,118,593	7
Sweet potato	611,586	4
Structural pest control	594,902	4
Almond	532,007	3
Outdoor grown transplant/propagative material	515,267	3
Walnut (English walnut, Persian walnut)	459,301	3
Outdoor grown cutflowers or greens	414,520	3
Total	11,508,799	72

<sup>&</sup>lt;sup>a</sup> DPR, 1999a. Total methyl bromide use in 1996 was 16,022,069 pounds

Table 3. Summary of methyl bromide usage in 1997 from the DPR database: Top ten uses.

<u>Usage</u>	Lbs methyl bromide	% Total
Strawberry (All or Unspecified)	4,050,264	26
Soil application, preplant-outdoor (seedbeds, etc	2,153,566	14
Outdoor container/field grown plants	922,659	6
Grapes, wine	897,380	6
Almond	893,299	6
Sweet potato	766,042	5
Grapes	579,120	4
Outdoor grown cutflowers or greens	545,718	3
Outdoor grown transplant/propagative material	509,527	3
Structural pest control	504,221	3
Total	11,821,796	76

<sup>&</sup>lt;sup>a</sup> DPR, 1999b. Total methyl bromide use in 1997 was 15,663,832 pounds.

Table 4. Summary of methyl bromide usage in 1998 from the DPR database:<sup>a</sup> Top ten uses.

Usage	Lbs methyl bromide	% Total
Strawberry (All or Unspecified)	4,252,131	31
Soil application, preplant-outdoor (seedbeds, et	c.) 1,522,344	11
Outdoor container/field grown plants	1,062,682	8
Outdoor grown transplant/propagative material	546,740	4
Sweet potato	541,923	4
Grapes, wine	478,247	4
Almond	459,260	3
Outdoor grown cutflowers or greens	429,620	3
Peppers (fruiting vegetable), (Bell, chili, etc.)	403,079	3
Structural pest control	360,618	3
Total	10,056,644	74

<sup>&</sup>lt;sup>a</sup> DPR, 2000a. Total methyl bromide use in 1998 was 13,569,875 pounds.

Table 5. Summary of methyl bromide usage in 1999 from the DPR database: a Top ten uses.

Usage	Lbs methyl bromide	% Total
Strawberry (All or Unspecified)	5,171,766	34
Soil application, preplant-outdoor (seedbeds, etc	c.) 2,159,084	14
Outdoor container/field grown plants	1,095,489	7
Grapes, wine	823,720	5
Outdoor grown transplant/propagative material	517,498	3
Peppers (fruiting vegetable), (Bell, chili, etc.)	544,962	4
Sweet potato	445,731	3
Walnut (English walnut, Persian walnut)	344,730	2
Almond	336,671	2
Peach	332,440	2
Total	11,772,091	76

DPR, 2000b. Total methyl bromide use in 1999 was 15,342,080 pounds.

# LABEL PRECAUTIONS/PERSONAL PROTECTIVE EQUIPMENT

All MB products are classified as Toxicity Category I pesticides bearing a signal word "Danger/Poison." The general precautionary statements for MB read: "Hazard to humans and domestic animals: Danger. Extremely hazardous liquid and vapor under pressure. Inhalation may be fatal or cause serious acute illness or delayed lung or nervous system injury. Do not breathe vapors. Liquid or excessive vapor can cause serious skin or eye injury, which may have a delayed onset. Do not get liquid on skin, in eyes, or on clothing." If the product contains chloropicrin, it further gives these statements: "This product contains chloropicrin as a warning odorant. Chloropicrin may be irritating to the upper respiratory tract, and even lower levels can cause painful irritation to the eyes, producing tearing. If these symptoms occur, leave the fumigation area immediately."

The labels also give the following restrictions: *Do not fumigate with MB when soil temperature is below approximately 50 °F at 6 inches, do not wear jewelry, gloves, goggles, tight fitting clothing, rubber protective clothing, or rubber boots when handling. MB and chloropicrin are heavier than air and can be trapped inside clothing and cause skin injury.* 

Product labels specify required personal protective clothing and equipment for workers. For example, applicators and other handlers must wear loose-fitting or well-ventilated long-sleeved shirts and long pants. The label requires respiratory protection when the air concentration level is above 5 ppm (20 mg/m³) at any time. DPR has established the target 24-hour TWA of 210 ppb (Nelson, 1992). The respiratory protection must be one of the following types: 1) a supplied air-respirator (MSHA/NIOSH approval number prefix TC-19C) or 2) a self-contained breathing apparatus (SCBA) (MSHA/NIOSH approval number prefix TC-13F). Under normal soil fumigation conditions, if the concentration of MB in the working area will not generally exceed 5 ppm, no respiratory protection is required. However, there is a possibility of a spill or leak during soil fumigation. Therefore, respiratory protection of a type specified above must be available and will be required for entry into the affected area in the event of a leak or spill.

#### **HUMAN ILLNESSES**

MB can cause serious human illness, especially when health protection and regulations are lax. In the past, MB was used as a refrigerant and a basic chemical in fire extinguishers. Some published literature revealed a history of serious illnesses caused by these uses or by accidental exposure to MB. Watrous (1942) reported a case where 33 out of 90 workers experienced systemic symptoms. These workers were involved in a packaging process where they placed liquid MB in glass ampoules, sealed the ampoules and inspected them for leakage. The air concentration of MB in the work area was generally less than 35 ppm. Workers experienced symptoms of anorexia, nausea, vomiting, headache, vertigo, difficulty in focusing the eye, lethargy, muscular pains, and dimness of vision. Johnstone (1944) reported 34 known cases of MB intoxication that developed in the date-packing industry in Indio, California. An estimated 15 to 20 more packers were absent from work for a period of two to 10 days but did not consult with a physician. The maximum allowable air concentration of MB at that time was 50 ppm. The high level of exposure was caused by leakage of chambers. Many of the fumigation chambers were not

constructed tightly enough to prevent leakage of MB into the workroom area. The majority of workers had neurologic disturbances involving vision, speech, tremors, and numbness of the extremities. There was a high incidence of mental confusion and some hallucinations. Depressive states lasted as long as five months. Other published reports revealed symptoms of different severity and fatalities among workers and residents (von Oettingen, 1946; Mezel *et al*, 1948; MacDonald, *et al.*, 1950; Ingram, 1951; Rathus and Randy, 1961; Longley and Jones, 1965; Alexeeff and Kilgore, 1983). Even though current California laws and regulations regarding the use of MB are more stringent than those in the 1940s and 1950s, illnesses still occur as a result of exposure to MB from various uses.

The Pesticide Illness Surveillance Program (PISP) of DPR maintains credible records of illnesses caused by MB. In California, physicians are required to report any illness or injury they suspect of being related to pesticide exposure. Data in Tables 6 and 7 show illnesses associated with exposure to MB and MB in combination with other pesticides from 1991 to 1999 (Mehler, 2001).

Table 6. Occupational and nonoccupational illnesses associated with exposure to methyl bromide alone in California (1991-1999).<sup>a</sup>

Methyl bromide alone	Illness/injury type				Total		
Activity	Systemic	Eye	Skin	Eye/skin	Def <sup>b</sup>	Prob <sup>c</sup>	Pos <sup>d</sup>
1. Occupational (occup.)							
Fumigation, field	1	0	11	1	10	2	1
Fumigation, tarpaulin	4	0	0	0	0	1	3
Fumigation, chamber	9	0	0	0	2	5	2
Exposed to drift	15	0	0	0	2	1	12
Residue and other	7	0	4	0	5	2	4
Emergency response	8	0	0	0	2	3	3
Exposed to concentrate	3	1	0	0	1	3	0
Total occupational	47	1	15	1	22	17	25
2. Nonoccupational							
Exposed to residues	15	3	0	0	2	15	1
Other	8	0	0	0	3	0	5
Total nonoccupational	23	3	0	0	5	15	6
Occup. + nonoccup.	70	4	15	1	27	32	31
Yearly average	7.8	0.4	1.7	0.1	3.0	3.6	3.4

<sup>&</sup>lt;sup>a</sup> Mehler, 2001.

The "definite (Def)" classification indicates the signs and symptoms exhibited by the affected person are such as would be expected to result from the exposure described and medical or physical evidence is available to substantiate the exposure.

<sup>&</sup>lt;sup>c</sup> The "probable (Prob)" classification indicates that there is close correspondence between the exposure and the illness experienced.

<sup>&</sup>lt;sup>d</sup> The "possible (Pos)" classification indicates some correspondence between the exposure described and the illness/injury experienced.

Table 7. Occupational and nonoccupational illnesses associated with exposure to methyl bromide in combination with other pesticides in California (1991-1999).<sup>a</sup>

Methyl bromide in combination with other pesticides	Illness/injury type				Total		
Activity	Systemic	Eye	Skin	Eye/skin	Def <sup>b</sup>	Prob <sup>c</sup>	Pos <sup>d</sup>
1. Occupational							
Fumigation, field	11	2	3	1	8	5	4
Fumigation, drift	8	1	0	0	1	5	3
Other residues	28	2	4	2	3	7	26
Emergency response	1	4	1	0	0	5	1
Total occupational	48	9	8	3	12	22	34
2. Nonoccupational							
Exposed to drift or residue	35	3	0	0	0	23	15
Total nonoccupational	35	3	0	0	0	23	15
Occup. + nonoccup.	83	12	8	3	12	45	49
Yearly average	9.2	1.3	0.9	0.3	1.3	5.0	5.4

<sup>&</sup>lt;sup>a</sup> Mehler, 2001.

The 9-year average illnesses associated with exposure to MB alone and MB in combination with other pesticides are 10.0 and 11.7 cases per year, respectively (Tables 6 and 7). The overall average is 21.7 cases per year. This average includes cases classified as "possible," accounting for about 40.8% of the overall average. The "possible" classification indicates some correspondence between the MB exposure described and the illness/injury experienced; whereas, the "definite" classification indicates the signs and symptoms exhibited by the affected person are such as would be expected to result from the exposure described and medical or physical evidence is available to substantiate the exposure. The "probable" classification indicates that there is close correspondence between the exposure and the illness experienced.

Affected people described a variety of illness/injury symptoms associated with exposure to MB alone or MB in combination with chloropicrin. Table 8 shows some symptoms reported by affected people in California from 1991 to 1999 for "definite" relationship category.

b The "definite (Def)" classification indicates the signs and symptoms exhibited by the affected person are such as would be expected to result from the exposure described and medical or physical evidence is available to substantiate the exposure.

The "probable (Prob)" classification indicates that there is close correspondence between the exposure and the illness experienced.

The "possible (Pos)" classification indicates some correspondence between the exposure described and the illness/injury experienced.

Table 8. Symptoms described by patients exposed to methyl bromide alone and in combination with chloropicrin in California (1991-1999).<sup>a</sup>

Illness/injury type	Observed symptoms <sup>b</sup>
Systemic/respiratory	Dizziness, lightheadedness, coughing, choking, nausea, headache, fever,
	shaking, sore throat, shortness of breath, vomiting, slurred speech, chest
	tightness and burning, disorientation, numbness on the cheek
Eye	Burning, irritation, tearing, double vision, itching, mild conjunctival
	inflammation, photophobia, moderate conjunctival irritation
Skin	Burning, pain, chemical burn, first and second degree burn, itching,
	painful swelling, redness, pruritic rash, blisters

<sup>&</sup>lt;sup>a</sup> Mehler, 2001.

# Evacuations after the use of MB:

From 1982 to 1999, there were six evacuations of people after the use of MB and chloropicrin (Richmond, 1997; Mehler, 2001). Summary of evacuations are as follows:

- 1. An evacuation occurred after a field was treated with MB and chloropicrin. The investigative report indicated that the apparent cause for the concentration of fumigants over the evacuation area was the lack of wind and a temperature inversion during and after the application, causing poor wind dilution and dispersion. As a result, 35 people were seen at local hospitals during evacuation. These people experienced systemic symptoms.
- 2. Seventy-one people at a labor camp were evacuated after a nearby nine-acre field was tarp fumigated. These people detected fumes and exhibited symptoms of exposure (tearing and burning eyes). This incident was caused by a gas leak. The seriousness of the gas leak involved two main factors, which were vandalism and poor wind movement.
- 3. Twenty-five people were evacuated from an area after four cylinders of MB fell off a pallet. One of the cylinders leaked gas. An employee was exposed and suffered from lightheadedness. Only this employee developed illness symptoms.
- 4. Approximately 100 people were evacuated from apartments when an adjacent apartment complex, which had been tarped and fumigated with MB, emitted white smoke from a vent pipe. It was found out later that the source of the smoke was the water heater closet in the back of the building. The Hazardous Materials Team later declared the building was free of toxic gases. There were no illness/injury from this incident.
- 5. One family of four was evacuated after they complained of odor and eye irritation subsequent to a field fumigation 434 feet upwind. The fire department responded to the complaint, and fire department personnel also experienced irritation. They noted that the problem was very spotty. It came and went, and was much more noticeable in some locations than at other nearby locations. The application of MB violated the applicable buffer zone requirement of 200 feet on other side of the field, but the people who lived within the buffer zone were not affected.

b symptoms are not arranged according to the degree of severity

6. Eighteen workers were evacuated from a packinghouse after two workers removed the custom locking caps from a methyl bromide cylinder. Accidentally, the valve was opened and released MB. Seven of the employees developed symptoms.

From 1982-1999, PISP received 25 reports involving people (generally seeking shelter) who entered enclosed areas treated with MB and one report involving a neighbor of the fumigated building. The atmosphere in these areas contained a lethal level of MB. Eighteen of the 24 people died. In 1997, one death occurred when MB diffused through unsealed conduits from a fumigated building to an occupied guest house a short distance away. The guest house occupant mentioned feeling poorly during the fumigation, and was found comatose and having seizures the day after the fumigation was complete. The blood bromine level was 27 mg/dl 5 days later. She died after 16 days in the hospital.

#### DERMAL TOXICITY AND SENSITIZATION

Symptoms observed in illness incidents indicate that liquid MB can cause severe eye and skin burns. The DPR's database does not have any submitted reports on dermal sensitization studies. Given the acute dermal toxicity of MB liquid, a sensitization study is not feasible.

#### ANIMAL/HUMAN METABOLISM

MB was rapidly biotransformed and readily excreted in rats after inhalation exposure (Bond *et al.*, 1985). In all tissues examined, over 90% of radioactivity was metabolites. The elimination half-life of radioactivity from the tissues was 1.5 to 8 hours. Almost 50% of the absorbed dose was excreted by the lungs as CO<sub>2</sub>. The pulmonary excretion was biphasic with half-lives of 3.9 hours and 11.4 hours. The half-lives of radioactivity were 9.6 hours and 16.1 hours in the urine and feces, respectively. In another inhalation study with rats, Bond *et al.* (1985) revealed that the percentages of the absorbed dose in the urine and feces were 23% and 2%, respectively. In other studies, Medinsky *et al.* (1985) and Jaskot *et al.* (1988) observed similar results (exhalation and excretion of the absorbed dose, and excretion half-lives) after inhalation exposure with rats.

In humans, the amount exhaled as  $^{14}\text{CO}_2$  ranged from 0.2 to 1.0% of the dose for mouth breathing, and 0.2% to 0.4% of the dose for nose breathing exposure when measured at the end of 2 hours of exposure and after 2 hours of clearance (Raabe, 1988). The net body retention for both exposure routes was 51.1% with a clearance half-life of 72 hours based on the amounts in the exhaled air and in the urine at 0.5 hour after inhalation exposure.

In rats after oral exposure, the distribution (as % of an absorbed dose) was 32% as <sup>14</sup>CO<sub>2</sub> and 4% as intact MB in exhaled air, 43% in the urine, and 14% in the carcass at 72 hours after exposure to MB (Medinsky *et al.*, 1984). Only 2% of the dose was found in feces. With intraperitoneal administration, the cumulative percentages of the doses in rats measured after 72 hours were: 45% as <sup>14</sup>CO<sub>2</sub> and 20% as intact MB in exhaled air, 16% in the urine, 1% in the feces, and 17% in the carcass (Medinsky *et al.*, 1984).

#### INHALATION UPTAKE/DERMAL ABSORPTION

# Inhalation uptake:

Inhalation uptake of MB was determined in beagles (Raabe, 1986), in humans (Raabe, 1988), and in rats (Medinsky *et al.*, 1985). Inhalation uptake of MB in adult nose-breathing beagle dogs was determined to be 39.8 percent (Raabe, 1986). In humans, the results were obtained from two males and two females in which uptake was evaluated by inhaling MB through mouth or nose. Means of the corrected inhalation uptake (observed uptake fraction x dead space correction factor) when breathing by mouth and nose are 52.1 and 55.4 percent, respectively (Raabe, 1988). Inhalation uptake of MB (1.6-9.0 ppm) in rats was determined to be about 48 percent, which is similar to inhalation uptake in beagles and humans (Medinsky *et al.*, 1985). Whenever it is necessary to estimate an absorbed dose from inhalation exposure, an inhalation absorption of 50% will be used. However, exposure estimates for MB in this document are shown as air concentrations instead of absorbed doses.

# Dermal absorption:

The DPR library database showed an article titled "Absorption of MB through the intact skin (Jordi, 1953)." Upon reviewing this article, there was no actual dermal absorption study of MB as indicated by the title of the article. This article reported the incidence of one fatal and two nonfatal cases of poisoning, which occurred after the fumigation of a flour mill. Results of the investigation revealed that the workers wore oxygen-supplying apparatus and there was adequate oxygen during the fumigation period. All workers experienced illness symptoms at least one hour after the fumigation, which took one hour and 30 minutes.

On March 26, 1985, Great Lakes Chemical Corporation submitted a request to the U.S. EPA for a waiver of dermal exposure data (TriCal, 1987). The registrant provided several reasons with the request. However, the U.S. EPA did not grant a waiver because the registrant provided insufficient evidence to the Agency for consideration. The registrant resubmitted a request after a meeting with the U.S. EPA personnel about the type of a closed system for MB application. The registrant claimed that workers would not be exposed to liquid MB under normal usage. Additionally, the only possible dermal exposure would come from a spill situation and under these conditions the inhalation route would still be the most important means of exposure (TriCal, 1987). Hence, a dermal absorption study is not needed for MB. On February 24, 1986, the agency granted the waiver of dermal exposure data based upon reasons that MB is applied in a closed system and the volatile nature of MB (boiling point = 4 °C). However, some questions still exist because there is a possibility that dermal absorption of MB is increased in areas with partly lipophilic character, such as armpit, groin, genitals, and the skin under the waist belt. This suggestion was substantiated by observations that skin lesions were limited to those areas where perspiration is relatively high (Zwaveling et al., 1987). However, these effects are only observed with extremely high ambient MB concentrations.

Dermal exposure may be important for those exposure scenarios in which dermal contact is the primary source of exposure, such as for workers who wear respiratory protection in areas with relatively high concentrations of MB. Based upon illness reports in the literature, there is potential for significant dermal exposure of workers who wear self-contained-breathing apparatus

(SCBA) in high MB concentration environment and work in the area for extended periods. Zwaveling et al. (1987) and Hezemans-Boer (1988) reported skin lesions in six workers eight hours after exposure for 40 minutes to high concentration of MB of approximately 40 g/m<sup>3</sup> or 10,000 ppm during the fumigation of an enclosed building. These workers were coveralls on top of normal daily clothing, PVC gloves, and work shoes. During the actual fumigation, these workers breathed pressurized air from a portable container through a tight fitting facemask. The skin lesions consisted of sharply demarcated erythema with multiple vesicles and large bullae. The lesions were limited to parts of the skin that were relatively moist and/or subjected to mechanical stress such as the armpits, groin, labia, vulva, penis, scrotum, rima ani, navel, and skin under the waistbelt. The mean plasma bromide concentration for samples collected immediately after the exposure and 12 hours after the exposure were 95  $\pm$  15 and 72  $\pm$  24 umol/L, respectively. It is possible that MB absorption is increased in this partly lipophilic (sebaceous glands) and partly hydrophilic (sweat glands) environment (Zwaveling et al., 1987). The percentage of dermal absorption could not be determined. Healing of the skin lesions of these workers occurred in 2 weeks. Deschamps and Turpin (1996) reported illnesses of two experienced fumigators who wore a cartridge respirator with activated charcoal. They entered a building where the concentration of MB was 17g/m<sup>3</sup>. Under the very high MB concentration environment, it is likely that the respirator was rapidly saturated with MB. It is for this reason that NIOSH does not recommend any air-purifying respirator for MB.

Dermal absorption of chemical vapors other than MB was studied. Four human volunteers (naked excepted shorts) were exposed to styrene vapors in the air within the concentration range of 1,300 to 3,200 mg/m³ for 2 hours (Wieczorek, 1985). These volunteers (3 men and 1 woman aged 25-35) breathed pure air from outside through a respirator. The results showed that dermal absorption of the styrene vapors contributed about 5% to the amount absorbed in the respiratory tract under the same conditions when the subjects did not wear a respirator. Riihimaki and Pfaffli (1978) studied percutaneous absorption of xylene, styrene, toluene, 1,1,1-trichloroethane, and tetrachloroethane vapors employing restricted numbers of human volunteers (n = 2-3 for each kind of vapor). The percutaneous absorption when the volunteers were exposed to moderate air concentrations of 300 and 600 ppm for 3.5 hours were about 0.1 to 2% of the amount estimated to be absorbed from the unprotected respiratory tract.

McDougal *et al.* (1985) studied dermal absorption of dibromomethane (DBM, 500 to 10,000 ppm) and bromochloromethane (BCM, 2,500 to 40,000 ppm) vapors in rats. The percentages of body burden, which was due to penetration of the skin, were 5.8% for DBM and 4.2% for BCM. The observed permeability constants in rats for styrene, xylene, toluene, perchloroethylene, benzene, halothane, hexane, and isoflurane were estimated to be two to four times greater than the human permeability constants calculated from the available literature data (McDougal *et al*, 1990). Based upon the difference in absorption of various chemical vapors in rats and humans, the percentage of body burden in humans was assumed to be 1.5 to 2.9% for DBM and 1.1 to 2.1% for BCM.

In conclusion, the dermal absorption of MB can be significant based upon reported illnesses of individuals with SCBA exposed to high concentration of MB for extended periods. Dermal exposures of other gases in humans such as styrene, xylene, styrene, toluene, 1,1,1-

trichloroethane, tetrachloroethane, dibromomethane, and bromochloromethane can be in the range of 0.1-5% of the unprotected respiratory exposure. However, there is no chemical-specific dermal absorption study for MB; we cannot meaningfully estimate dermal exposure at this time.

#### FARM COMMODITY RESIDUES

MB is used to fumigate fresh fruits, vegetables, and raw agricultural and processed food commodities. These treatments are needed to control pests and to comply with U.S. import requirements and quarantines of other nations. Applications are usually made to fresh produce before it is loaded for export or to harvested crops before they are processed further. If the raw or processed commodity is stored for an extended period of time, additional fumigations may be necessary to control infestations of Indian meal moth and other pests. MB applications are made by treating the whole structure containing the commodity, covering the commodity with tarps or placing the commodity in a fumigation chamber. The treatment is a function of the application rate of the gas (pounds (Lbs) of MB per 1,000 ft<sup>3</sup> of commodity or space being treated), temperature of the commodity, exposure time and the load factor (percentage of the chamber area filled by the commodity). After the exposure period has expired, the commodity is aerated to remove the gas. Aeration can be done passively where the chamber doors are left open or the tarps are removed to allow the gas to dissipate. It can involve active ventilation where fans are used to exhaust the gas from chambers or to blow through the treated commodity.

The data in the Table 9 were derived from studies concerning the fumigation of various commodities. MB residues were detected in treated commodities using the headspace analytical method (King *et al.*, 1981) with the exception of treated wheat, which was analyzed using the derivative method (Fairall and Scudamore, 1980), the reflux method (Malone, 1970) and FDA methodology (CDFA, 1984b). Half-lives were calculated for the rates of dissipation of the organic bromide residues remaining after each treatment. These values were derived from the linear regression analysis of the time versus residue data points presented in the studies. The natural log of 2 was divided by the rate constant (slope) to estimate the half-life from the start of aeration.

Table 9 shows commodities that are representative of general fumigation. This table also contains information indicating how physical conditions and aeration can affect the amount of organic bromide residues left in the treated commodity. The temperature at which the commodity was treated and subsequently aerated and stored was the primary factor in determining the rate of dissipation of MB residues left in the treated commodity. As demonstrated in the residue data for "cherries," the greater the temperature, the more rapid the dissipation rate as expressed in the shorter half-life. This relationship is expressed by the following Arithmetic equation:  $\log(\text{rate constant}) = a + b(1/K)$ , where K is temperature in degrees Kelvin. Cherries fumigated at lower temperatures had greater amounts of organic bromide residues at the start of aeration than that treated at the same rate, but at a higher temperature.

The majority of the studies were conducted in the laboratory with fumigation chambers ranging in size from 1-28 ft<sup>3</sup>, with almonds and walnuts fumigated in larger chambers (100-110 ft<sup>3</sup>). Only the strawberry and wheat studies involved sampling for MB residues under actual commercial

usage. Studies were conducted to test the hypothesis that chambers of various sizes might produce different dissipation rates. There may be some reservations regarding the use of this data to estimate commercial use conditions. MB fumigation studies were conducted comparing commercial and laboratory treatments of commodities at the same rates. The concentrations of MB were monitored in chambers of various sizes (0.028-5,494 m³) during an inshell almond fumigation study (Hartsell *et al.*, 1992). The levels of fumigant from an application of 24 g/m³ at 26 °C for four hours were similar at various times: 28.3 L (0.028 m³) chamber, 14.8-15.1 g/m³ at 1.0 hour, 13.1-13.5 g/m³ at 4 hours and the 5,494 m³ chamber, 16.8 g/m³ at 1.0 hour, 12.5 g/m³ at 4 hours. A similar study was conducted during the fumigation and subsequent aeration of raisins (Hartsell *et al.*, 1992). The regression analysis of the data points derived comparable rate constants (slopes) for the dissipation rates for up to eight days for the lab and commercial chambers.

A 1975 study of tarp fumigations with hull almonds in piles at the harvest site observed the temperature variability that occurs when commodities are fumigated outdoors (Nelson *et al.*, 1975). During the 24-hour fumigations, temperatures ranged from 69-79 °F at the bottom of the pile near the edge to 83-120 °F for one of the top corners at a depth of 1-2 feet. This temperature variability makes it difficult to predict the dissipation rate for the organic bromide residues.

The almond fumigation study (Hartsell *et al.*, 1984b) researchers observed that wooden bins with slots cut in the sides allowed the MB gas to dissipate faster than bins with solid sides. Harris *et al.* (1983) found that polystyrene foam boxes desorbed larger quantities of MB gas compared to cartons constructed of wood or fiberboard. When a fumigation chamber (49.6 ft<sup>3</sup>) containing empty polystyrene foam grape boxes was fumigated, aerated and resealed, MB levels in the chamber reached a maximum of 3.0 g/m<sup>3</sup>. Sinclair and Lindgen (1952) noted that during the fumigation of empty flats, the excelsior packing material absorbed 20% of the applied MB in the chamber.

Table 9. A log-linear regression analysis of residue data over time from methyl bromide chamber fumigation of various commodities.<sup>a</sup>

	F		tion me	ethod	Storage	Rate	Residues at	
Crop	Rateb		Temp.			constant <sup>c</sup>	aeration <sup>d</sup>	$t_{1/2}^{e}$
<del></del>		(hr)	(°C)		(°C)		(ppm)	(hours)
In shell almonds (shells)	1	12	10	70-75	n/a	0.054	46.7	12.8
In shell almonds (shells)	1	8	15.6	70-75	n/a	0.051	17.3	13.6
In shell almonds (shells)	1	4	26.7	70-75	n/a	0.044	15.5	15.7
In shell almonds (meats)	1	12	10	70-75	n/a	0.018	9.5	38.4
In shell almonds (meats)	1	8	15.6	70-75	n/a	0.027.	4.4	26.4
In shell almonds (meats)	1	4	26.7	70-75	n/a	$0.023^{J}$	4.9	31.2
Almond meats in cartons	1	8	15.6	70-75	n/a	0.047	13.4	14.8
In shell walnuts (meats) <sup>f</sup>	3.5	4	15.6	50-55	1.7	0.127	56.5	132
In shell walnuts (meats) <sup>f</sup>	3.5	4	15.6	50-55	10	0.162	50.2	103.2
In shell walnuts (meats) <sup>f</sup>	3.5	4	15.6	50-55	32	0.563	31.0	28.8
Fresh strawberries <sup>g</sup>	3	3	18.3	n/r	n/a	1.149	26.4	0.60
Fresh strawberries <sup>h</sup>	3	3	18.3	n/r	1.1	$0.037^{J}$	n/a	18.7
Lemons	2.75	2	21	50	10	0.021	2.2	33
Grapefruit	4	2	20	80	24	0.085	26.8	8.2
Wheat in storage	1.5	24	21	100	21	$0.035^{J}_{i}$	0.111	19.8
Wheat in storage	1.5	24	21	100	21	$0.049^{1}$	0.519	14.2
Wheat in storage	1.5	24	21	100	21	$0.087^{^{J}}$	0.648	8.0
Wheat in storage	1.5	24	21	100	21	0.061	1.149	11.3
Avocados (Hass) whole fruit	t 2	2	20	40	22	$0.108^{J}$	3.0	6.4
Avocados (Hass) whole fruit	t 2	4	20	40	22	$0.112^{J}$	4.4	6.2
Cherries	3	2	3	32	3	0.296	83.5	2.3
Cherries	3	2	9	32	9	0.398	76.0	1.7
Cherries	3	2	23	32	23	0.636	59.2	1.1
In shell pistachio meats <sup>i</sup>	1	24	15.5	80	15.5	0.016	12.5	62.5
In shell pistachio meats <sup>i</sup>	1.5	24	15.5	80	15.5	0.014	20.6	49.5
In shell pistachio meats <sup>i</sup>	1.5	24	26.6	80	26.6	0.013	10.6	53.3
In shell pistachio meats <sup>i</sup>	3.5	24	26.6	80	26.6	0.014.	20.1	49.5
Peaches	3	3	21	50-60	2.5	$0.168^{J}$	15.4	4.1
Plums	3	3	21	50-60	2.5	0.045	34.1	15.4
Pears	3	3	21	50-60	2.5	0.047	22.7	14.8
Raisins	1.5	24	10	50	10	0.005	1.3	139
Dried apricots in bulk	1.5	24	10	50	10	0.023	4.1	30.1
Dried apricots in packages	1.5	24	10	50	10	0.011	7.3	63
Nonpitted prunes in bulk	1.5	24	10	46	10	0.018	4.8	38.5
Pitted prunes in bulk	1.5	24	10	46	10	$0.018^{1}$	4.9	38.5
Brown rice in 2 lb boxes	1.5	16	21	not known	21	$0.046^{j}$	143.0	15.0
Milled rice in 2 lb boxes	1.5	16	21	not known	21	$0.064^{^{\mathrm{J}}}$	1.9	10.8

n/a-not applicable or no data available; n/r-not reported

Table 9 (cont.). A log-linear regression analysis of residue data over time from MB chamber fumigation of various commodities.

- <sup>a</sup> References for various commodities are:
  - 1. almonds-Hartsell et al., 1984b.
  - 2. pistachios-Hartsell et al., 1986.
  - 3. walnuts-Hartsell et al., 1984a.
  - 4. avocados-Singh et al., 1982.
  - 5. cherries-Sell et al., 1987.
  - 6. grapefruit-King et al., 1981.
  - 7. prunes-Obenauf, 1992.
  - 8. peaches-Tebberts et al., 1983.
- b pounds MB per 1,000 ft<sup>3</sup>.

- 9. pears-Tebberts et al., 1983.
- 10. plums-Tebberts et al., 1983.
- 11. strawberries-CDFA, 1984a.
- 12. wheat-CDFA, 1984b.
- 13. lemons-Soderstrom et al., 1991.
- 14. apricots-Hartsell et al., 1992.
- 15. rice-Anonymous, 1992.
- 16. raisins-Hartsell et al., 1992.
- same as the regression coefficient (slope of the regression line) for natural log of MB concentration as a function of time.
- d estimated residues at start of aeration. Residues were calculated based on y-intercept of the regression line.
- e half-life  $(t_{1/2}) = \log_2/\text{rate constant}$ .
- f fumigated at reduced pressure of 100 mm Hg.
- g calculated as the mean from two replications.
- calculated with 1.0 ppb as 50% of the minimum detectable level.
- mean value of residues after three sequential treatments made at the listed rate, 20 days apart. the regression performed for this crop was found to be insignificant (with P-value >0.05).

Several fumigation trials observed the MB residues remaining in commodities when two different percents of load (10% versus 50%) were used in the chamber for the same treatment (Hartsell *et al.*, 1992). A t-test of the differences in residues from the two load factors indicated that the percent load may affect the amount of residues remaining in the fumigated commodity. However, the t-test may not be an appropriate method for determining if the difference is significant because the samples were not randomly taken.

#### **EXPOSURE ASSESSMENT**

MB exposure estimates include those determined for workers during fumigation of preplant soil, agricultural commodities or structures as well as for residents or persons who live or work at the buffer zone distance of commodity or field fumigation. Ambient MB concentrations in the high use counties (Monterey, Santa Cruz and Kern) are also shown in this document. Air concentrations of MB at specified periods are shown as ppb or ppm (parts per million) whenever they are appropriate.

Some of the exposure estimates are grouped into acute and nonacute exposures depending on the nature of each work task or exposure scenario. Acute exposure is the exposure that occurs daily or within 24 hours. Nonacute exposures, as used in this document, are those exposures that occur in these specified periods: 7 days (subacute), 90 days (subchronic), and 365 days (chronic). Definitions of subchronic and chronic exposures are adopted from Sanders (1998). Duration (daily exposure time, e.g. 4 hours per day) and frequency (days of exposure in a specified period, e.g. 45 days in a 90-day period) of exposure for each work task or exposure scenario are used to determine whether the exposure is acute or nonacute exposure. These exposure scenarios also reflect toxicological endpoints observed in experimental animals as determined by DPR.

Calculations of exposure rely on factors, including application rates, work periods specified in the current California permit conditions and duration and frequency of exposure. Types of tarpaulins, application equipment, and injection depth are used in the permit conditions to determine the maximum daily work time for each type of soil injection fumigation. DPR requested MB registrants to provide duration and frequency of exposure for acute and nonacute exposures (Donahue, 1997). Several registrants provided some data as requested. Consequently, default duration and frequency of exposure for many exposure scenarios were generated from data obtained from various sources and the use of professional judgment (Haskell, 1998a, 1998b). These default values are shown in Appendix A (Table 12).

As shown in the previous section on formulations, many MB products contain chloropicrin. However, the exposure assessment of chloropicrin has not been initiated at this time. This chemical has been placed in the high priority list under the Birth Defect Prevention Act of 1984. The exposure assessment may be initiated depending on the priority of the Department's risk assessment.

# Exposure calculation procedures:

MB exposure estimates are calculated for acute and nonacute exposures for applicable exposure scenarios. In each case, the air concentration is shown as the 24-hour TWA. (*Notes:* Lbs a.i. as used in this document is equivalent to Lbs MB unless mentioned otherwise. Lbs formulated product may include only MB or MB and chloropicrin.)

# a) Acute exposures

Procedures used to estimate the 24-hour TWA concentration are as follows:

a.1) Volume of air sample at standard temperature and pressure of 25 °C and 760 mm Hg

$$VS = \frac{V \times P \times 298}{760 \times (T + 273)}$$

where VS is volume of air (L) at standard conditions,

V is volume of air sample (L) as measured,

P is measured barometric pressure in mm Hg, and

T is measured temperature of air in °C,

# a.2) Calculation of MB concentrations (ppm) in air

MB (ppm) = 
$$\frac{\mu g \times 24.45}{VS \times 94.94}$$
 =  $\frac{\mu g \times 0.2576}{VS}$ 

Where one mole of MB occupies 24.45 liters at 25 °C and the molecular weight is 94.94.

# a.3) Conversion of MB from µg/m³ to ppb and vice versa

1 ppb = 
$$\frac{24.45}{94.94}$$
 x  $\mu g/m^3$  =  $0.26 \text{ x } \mu g/m^3$   
1  $\mu g/m^3$  =  $\frac{94.94}{24.45}$  x ppb =  $3.88 \text{ x ppb}$ 

# a.4) Calculation of the 24-hour TWA concentration

$$TWA = \frac{C_1T_1 + C_2T_2 + C_nT_n}{24 \text{ hours}}$$

where TWA is MB concentration (ppb, ppm,  $\mu g/m^3$ , or  $mg/m^3$ ,

C is concentration of MB during an increment of exposure, and

T is incremental exposure time in 24 hours.

# b) Nonacute exposures

The nonacute exposure estimates shown in this document represent subacute, subchronic, and chronic exposures. The underlying reason for nonacute exposure is that workers or residents may be exposed to airborne MB either continuously or intermittently for longer than 24 hours. Exposure duration and frequency for nonacute exposures were used to estimate exposure. Exposure for the subacute or subchronic exposure period is that period during the maximum or peak use of MB for fumigation purposes. Basically, the nonacute exposure estimates are determined from daily exposures either as acute, subchronic, or chronic exposure as shown below.

Nonacute exposure estimate (ppb) = <u>Daily exposure (ppb) x Days of exposure (days)</u> Exposure period (7, 90 or 365 days)

# Definitions:

The "**High Barrier**" tarpaulin must have a permeability factor of less than 8 milliliters MB per hour, per square meter, per 1,000 ppm of MB under tarp at 30 °C. Any polyethylene tarp of 6-mil thickness or greater meets this criterion.

The "**Very High Barrier**" tarpaulin must have a permeability factor of less than 5 milliliters MB per hour, per square meter, per 1,000 ppm of MB under tarp at 30 °C.

# Availability of worker exposure studies:

Before 1992 studies were conducted using then-current soil injection equipment, which often resulted in high air concentrations of MB near the worker's breathing zone. These studies are summarized in (a) below. Subsequently, DPR required registrants to conduct many exposure studies in order to determine short-term air concentrations of MB in various uses and exposure scenarios. Starting in 1992, registrants of MB conducted exposure monitoring studies during the fumigation of preplant soil, agricultural commodities, and other structures. Submitted reports indicated that many studies were not conducted in compliance with Good Laboratory Practice (GLP) standards as indicated in 40 CFR 160 (U.S. EPA, 1998). The main reason why these studies were not in GLP compliance was due to no valid field or laboratory fortification recovery study. Field exposure studies conducted in and after 1992 are summarized in (b) below. Many of these studies were used to estimate exposures for risk assessment.

# a) Summary of MB exposure studies conducted before 1992

In 1987, TriCal, Inc. submitted reports of several worker exposure studies (TriCal, 1987). The first data set consisted of exposure data generated during fumigations of a flour mill, processing and handling silo, grain silo, shipping container, transportation vehicle (barge loaded with oak logs), furniture covered with tarpaulin, and flat storage fumigation (corn, soybeans). The analytical and exposure monitoring methods were based on NIOSH method No. S372. Air samples were collected from the worker's breathing zone using a sampling train that consisted of two 600 mg coconut shell charcoal sampling tubes and a personal air sampling pump. The principle of quality control/quality assurance was observed during the studies. The analytical recovery for MB ranged from 95 to 117%. Results were reported as the 8-hour TWA (Table 10). The application rates for most uses were not noted, but the report indicated that label instructions were followed.

Table 10. Air concentrations of methyl bromide near the worker's breathing zone.<sup>a</sup>

				8-hr TWA (ppm)
	Type of fumigation	Work task	n	Average ± STDEV (range)
1.	Flour mill			, <u>, , , , , , , , , , , , , , , , , , </u>
a)	Applicators opened gas tanks located	Applicators	9	$4.1 \pm 4.4 (0.04-13)$
	inside the building.	Aerators	7	$7.8 \pm 6.9 (0.01-15)$
		Tape removers	1	0.4
b)	Applicators opened gas tanks located	Applicators	4	$0.2 \pm 0.27 \ (0.06 \text{-} 0.61)$
	outside the building.	Aerators	3	$5.5 \pm 7.3 (1.1-14)$
2.	Processing and handling silo	Applicators	3	$7.3 \pm 5.0 \ (2.7 - 12.6)$
	(enclosed conveyer and storage bins)	Aerators	2	0.07 (0.03 and 0.1)
3.	Grain silo, elevator, or bin	Applicators	3	$0.5 \pm 0.1 \ (0.4 - 0.6)$
		Aerators	3	$0.2  (ND)^b$
		Grain loaders	2	$0.2  (ND)^{b}$
4.	Shipping containers (trailers or rail	Applicator	1	0.02
	cars)	Aerator	1	6.8
5.	Transportation vehicle (barge loaded	Applicator	3	$0.6 \pm 0.3 \; (0.05 \text{-} 0.9)$
	with oak logs)	Supervisor	1	0.04
		Inspectors	1	0.02
		Aerators	2	16.1 (7.1 and 25)
		Tarp removers	2	0.4 (0.3 and 0.5)
6.	Tarpaulin (wooden furniture and a	Applicators	2	0.1
	pallet of flour)	Tarp remover	1	0.2
		Aerator	1	1.3
7.	Flat storage building (filled to the	Applicator	3	$0.25 \pm 0.1 \ (0.2 \text{-} 0.3)$
	ceiling with corn, soybeans)	Helpers	2	0.1 (0.02 and 0.2)
		Aerators	2	0.1 (0.02 and 0.2)

<sup>&</sup>lt;sup>a</sup> n is number of replicates; TWA is Time-Weighted Average; STDEV is standard deviation.

TriCal, Inc. also conducted worker exposure studies to determine exposures of tractor drivers and co-pilots to MB during tarpless bed fumigation (TriCal, 1990). Application rates ranged from 50 to 360 pounds MB per acre and the injection depth ranged from 4 to 18 inches under the soil surface. Air concentrations at various distances from treated fields were also measured. The application of MB in these studies presumably used unmodified application equipment, unlike those currently used to reduce worker exposure. Exposure ranges (ppm) for drivers obtained from four studies were 0.009-1.500 (carrots), 2.952-4.772 (potatoes), 0.648-1.704 (seedbed), and 1-2.1 (broccoli), and those for co-pilots were 0.270-1.524 (carrots), and 2.544-3.212 (seedbed). These air concentrations are high compared to the current target exposure level of 210 ppb for acute toxicity. The downwind air concentrations, measured 60 to 200 feet from treated fields, ranged from 0.03-0.211 ppm.

Minimum detectable level (MDL) ranged from 0.01 to 0.4 ppm depending on sample volume; one-half of the high MDL or 0.2 ppm was used whenever the result indicated "nondetects (ND)."

TriCal, Inc. also submitted several other studies that measured MB air concentrations near the worker's breathing zone (TriCal, 1987). These studies are listed below:

- 1. Deep tarpless application, Wasco, California. April 2, 1986. DPN 123-099, record number 64750.
- 2. Deep tarpless application, Delano, California. May 30, 1986. DPN 123-099, record number 64750.
- 3. Tarped field fumigation, Ducor, California. April 2, 1984. DPN 123-099, record number 64750.
- 4. Driscoll chamber fumigation, Watsonville, California. March 26, 1984. DPN 123-099, record number 64750.
- 5. Driscoll chamber fumigation (strawberries for export), Watsonville, California. July 18, 1984. DPN 123-099, record number 64750.
- 6. A study of the inhalation exposure of workers to MB and chloropicrin during preplant soil fumigations (shallow injection) in 1982 A preliminary report. DPN 123-099, record number 64751 (or HS-1076, June 10, 1983, DPR).
- 7. A study of the inhalation exposure of workers to MB during preplant soil fumigations (shallow injection) in 1980 and 1981. DPN 123-099, record number 64752 (or HS-900, May 20, 1982, DPR).
- 8. A study of the levels of MB and chloropicrin in the air downwind from a field during and after a preplant soil fumigation (shallow injection) A preliminary report. DPN 123-099, record number 64753 (or HS-1061, April 15, 1983, DPR).

Results from these studies are not employed for estimation of worker exposure due to one or more reasons listed below.

- 1. The report does not contain adequate information concerning fumigation method, sample collection and processing, and analysis (QA/QC) to ensure correct calculation of the TWA air concentrations.
- 2. The study used unacceptable analytical methods.
- 3. There are better studies conducted in and after 1992.
- 4. The studies conducted before 1992 do not reflect current work practices.

# b) Summary of MB exposure studies conducted after 1992

MB exposure estimates and results of grouping of exposure estimates are shown in Tables 11, 12, 13 and 14. Table 11 shows exposures for handlers and other workers calculated as acute, subacute, subacute, subchronic and chronic exposures. Table 12 shows acute exposures for persons at the buffer zone distance. Table 13 shows results of grouping of some acute exposures. Table 14 shows ambient MB concentrations in three high use counties in CA. Details of studies and calculations are presented in Appendices B, C and D. Factors concerning duration and frequency of exposure for various work tasks and exposure scenarios are shown in Appendix A (Table 12).

Table 11. Summary: Acute and non-acute exposure estimates of persons in California to methyl bromide\*.

		te exposu			cute exp.			onic exp			Chronic exp. (ppl		
Number/		24-hour p			-day peri			-day peri			5-day pe		
Type of application (Data from Table)**	Avg. S	STDEV	Range***	Days	Avg.	STDEV	Days	Avg.	STDEV	Days	Avg.	STDEV	
a) Shallow shank-tarped soil injection fumigation (T. B.1)     Applicators: Noble plow shanks	111	98	3-303	6	95	84	40	49	44	n/a	n/a	n/a	
a) Shallow shank-tarped soil injection fumigation (T. B.2) Co-pilots: Noble plow shanks	224	152	34-518	6	192	130	40	100	68	n/a	n/a	n/a	
a) Shallow shank-tarped soil injection fumigation (T. B.3) Shovelmen: Noble plow shanks (by growers)	147	135	52-515	3	63	58	n/a	n/a	n/a	n/a	n/a	n/a	
a) Shallow shank-tarped soil injection fumigation Tarp removers (by PCOs) (T. B.4) Tarp removers (by growers) (T. B.5)	835 278	596 199	3-1659 1-553	5 2	596 79	426 57	55 n/a	510 n/a	364 n/a	n/a n/a	n/a n/a	n/a n/a	
b) Nontarp deep shank injection fumigation (T. B.6) Applicators Co-pilots Cultipacker	154 49 99	n/a n/a n/a	126&181 n/a n/a	6 6 6	132 42 85	n/a n/a n/a	40 40 n/a	68 22 n/a	n/a n/a n/a	n/a n/a n/a	n/a n/a n/a	n/a n/a n/a	
<ul> <li>b) Nontarp deep shank injection fumigation (improved) (T. I Applicator Cultipacker</li> </ul>	3.7) 57 70	n/a n/a	n/a n/a	6 6	49 60	n/a n/a	40 n/a	25 n/a	n/a n/a	n/a n/a	n/a n/a	n/a n/a	
c) Nontarp deep shank injection fumigation (T. B.7) Appl: Basic + a second tractor with a disc Disc driver: Basic + a 2nd tractor with a disc Applicator: Basic + a cultipacker Supervisor: Basic + a cultipacker Cultipack.: Basic + a cultipacker (by growers)	88 512 94 67 34	n/a n/a n/a n/a n/a	n/a n/a 22&165 n/a 10&58	6 6 6 6	75 439 81 57 29	n/a n/a n/a n/a n/a	40 40 40 40 n/a	39 228 42 30 n/a	n/a n/a n/a n/a n/a	n/a n/a n/a	n/a n/a n/a n/a n/a	n/a n/a n/a n/a n/a	
d) Nontarp deep shank injection fumigation (T. B.8) Applicator: With 4 forward curved shanks Cultipack: 4 forward curved shanks (grower)	7 7	n/a n/a	n/a n/a	6 6	6 6	n/a n/a	40 n/a	3 n/a	n/a n/a	n/a n/a	n/a n/a	n/a n/a	
e) Shallow shank-tarped bed fumigation (T. B.9) Appl: Conv.+ raised platform&inj. 8" Co-pilots: Conv.+ raised platform&inj. 8"	80 104	n/a n/a	n/a 98&111	6 6	69 89	n/a n/a	40 40	36 46	n/a n/a	n/a n/a	n/a n/a	n/a n/a	
Applicators: Conv. + closing shoes Co-pilots: Conv. + closing shoes * acute exposure is the exposure that occurs daily or within 2	44 167	n/a n/a	n/a 125&209	6 6	38 143	n/a n/a	40 40	20 74	n/a n/a	n/a n/a	n/a n/a	n/a n/a	

<sup>\*</sup> acute exposure is the exposure that occurs daily or within 24 hours; subacute exposure is the exposure that occurs in a seven-day period; subchronic exposure is the exposure where days of exposure is 30 days or longer in a 90-day period; chronic exposure is the exposure where days of exposure is 120 days or longer in a 365-day period.

\*\* where applicable, the daily average and standard deviation for subchronic and chronic exposure were taken from the table as indicated for use in the calculation of subchronic and chronic exposures shown in this table.

<sup>\*\*\*</sup> when there are only two data points, these two data points are shown as, e.g. 34&24, and the standard deviation was not calculated.

Notes: 1. A standard deviation (STDEV) was not calculated when there were only two exposure values.

<sup>2.</sup> Abbreviations: T. = (from) Table; exp. = exposure; by growers or pest control operators (PCOs) = employed by growers or PCOs; Avg. = average; conv. = conventional; inj. = injection; Tr. = tractor; n/a = not applicable (data are not available or cannot be calculated).

Table 11. (continued 1). Acute and non-acute exposures of persons in California to methyl bromide\*.

	Acı	ite expos	ure (ppb)	Sub	acute exp.	(ppb)	Subchi	ronic exp	. (ppb)	Chronic exp. (ppb)			
Number/		/24-hour			7-day peri			-day peri		/365-day period			
Type of application (Data from Table)**	Avg.	STDEV	Range***	Days	Avg.	STDEV	Days	Avg.	STDEV	Days	Avg.	STDEV	
f). Shallow shank-tarped bed fumigation (T. B.10)													
Driver: Tr. was equipped for fum. (by PCOs)	28	n/a	n/a	6	24	n/a	40	12	n/a	n/a	n/a	n/a	
Appl: Tractor was equipped for MB fum.	45	n/a	n/a	6	39	n/a	40	20	n/a	n/a	n/a	n/a	
Tape layer: Tr. was equipped for MB fum.	65	n/a	n/a	3	28	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
Driver: Tractor was equipped for laying tarp	4	n/a	n/a	6	3	n/a	40	1.8	n/a	n/a	n/a	n/a	
Co-pilot: Tr was equipped for laying tarp	34	n/a	4&65	6	29	n/a	40	15	n/a	n/a	n/a	n/a	
g). Shallow shank, tarped-bed fumigation (T. B.11)													
Applicator	2	n/a	n/a	6	2	n/a	40	1	n/a	n/a	n/a	n/a	
Co-pilot	32	n/a	31&32	6	27	n/a	40	14	n/a	n/a	n/a	n/a	
Shovelman (by growers)	0.6	n/a	0.6&0.6	3	0.3	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
h). Tarp shallow with Noble plow shanks (T. B.12)													
Cutter: From broadcast appl. (by growers)	27	45	2-79	2	8	13	n/a	n/a	n/a	n/a	n/a	n/a	
Cutter: From broadcast appl. (by PCOs)	82	134	3-237	2 5	59	96	30	27	45	n/a	n/a	n/a	
Puller: From broadcast appl. (by growers)	11	31	1-108	2	3	9	n/a	n/a	n/a	n/a	n/a	n/a	
Puller: From broadcast appl. (by PCOs)	33	92	3-324	5	24	66	30	11	31	n/a	n/a	n/a	
i). Tarp shallow with Noble plow shanks (T. B.13)													
From use of high barrier (HB) tarp													
Cutter: By PCOs	78	n/a	n/a	5	56	n/a	30	26	n/a	n/a	n/a	n/a	
Remover: Tractor driver (by PCOs)	343	n/a	n/a	5	245	n/a	30	114	n/a	n/a	n/a	n/a	
Remover: Basketman (by PCOs)	325	n/a	n/a	5	232	n/a	30	108	n/a	n/a	n/a	n/a	
Remover: End puller (by PCOs)	7	n/a	n/a	5	5	n/a	30	2	n/a	n/a	n/a	n/a	
Cutter (by growers)	26	n/a	n/a	5	19	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
Remover: Tractor driver (by growers)	114	n/a	n/a	5	81	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
Remover: Basketman (by growers)	108	n/a	n/a	5	77	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
Remover: End puller (by growers)	2	n/a	n/a	5	1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
2.a. Worker exposure assessment during potting soil fumiga	tion (no u	sable dat	a)										
2.b. Greenhouse soil fumigation (T. B.14)	I `		,										
Tarp venters	0.009	0.02	0.00006-0.03	1	0.0013	0.003	n/a	n/a	n/a	n/a	n/a	n/a	
Tarp removers	0.95	0.89	0.23-2.2	1	0.1357	0.1271	n/a	n/a	n/a	n/a	n/a	n/a	
3. Fumigation of grain products (chambers, sea containers) (	T. B.15)												
Initiation of aeration of sea containers/truck trailer													
Aerator	0.6	0.41	0.13-0.85	5	0.43	0.29	45	0.33	0.22	180	0.25	0.17	
Initiation of aeration of tarpaulin fumigation						/			<b>-</b>			,	
Aerator	0.025	0.041	0.001-0.07	5	0.02	0.03	45	0.01	0.02	180	0.01	0.02	
Emptying sea containers/truck trailers		2.0.1	2.231 0.07		J.U.	0.05			0.02	-00		0.02	
Forklift driver	16	24	2-43	5	11	17	45	4	6	180	4	6	
Emptying non-certifying fumigation chambers	1.0		2 43	3		1/	.5	•	· ·	100	-	Ü	
Forklift driver	6	2	4-8	5	4	1	45	2	1	180	1	0.5	

Table 11. (continued 2). Acute and non-acute exposures of persons in California to methyl bromide\*.

		ute exposu		Suba	cute exp.	(ppb)	Subchr	onic exp	. (ppb)	Chro	nic exp. (	ppb)
Number/		/24-hour p			-day peri			-day peri			5-day per	od
Type of application (Data from Table)**	Avg.	STDEV	Range***	Days	Avg.	STDEV	Days	Avg.	STDEV	Days	Avg. S	STDEV
4. Fumigation of dried fruit and tree nut products (T. B.16)												
Chamber (raisins):				_								
Fumigators	63	n/a	19&107	6	54	n/a	63	44	n/a	150	17	n/a
Aerators	47	n/a	30&64	6	40	n/a	63	33	n/a	150	13	n/a
Clear chambers 1-2	1434	n/a	1406-1463	6	1229	n/a	63	1004	n/a	150	393	n/a
Stem pickers	28	n/a	26&30		24	n/a	63	20	n/a	150	12	n/a
Forklift driver	3	n/a	n/a	6	3	n/a	63	2	n/a	150	0.4	n/a
Hopper operator	19	n/a	n/a	6	16	n/a	63	13	n/a	150	8	n/a
Area sampling:												
Fumigation chambers	88	n/a	n/a	6	75	n/a	63	62	n/a	150	24	n/a
Fumigation cage	54	n/a	n/a	6	46	n/a	63	38	n/a	150	15	n/a
Leak checkers-chambers 4-5	4	n/a	2&6	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Aeration-chambers 4-5	116	n/a	47&186	6	99	n/a	63	81	n/a	150	32	n/a
Clearing-chambers 4-5	46	n/a	26&66	6	39	n/a	63	32	n/a	150	13	n/a
Hopper areas	8	n/a	2&13	6	7	n/a	63	6	n/a	150	3	n/a
Stem picker	27	3	24-30		23	3	63	19	2	150	11	1
5. Measurement of MB exposure to the fumigators, forklift d		·		orkers (no	o usable o	data)						
Methyl bromide air monitoring studies at a walnut process     a) Worker exposure studies	ing facil	ity (T. B.17	7)									
	34	m/a	24&44	6	29	m/o	75	28	n/a	n/a	n/a	<b>m</b> /o
Bulk packaging	208	n/a 155	1-404	6	178	n/a 133	75 75	173	129	n/a n/a	n/a n/a	n/a n/a
Cleaning plant	208 87	32		_	75	27	75 75			180	11/a 19	11/a 7
Fumigatorium	87 44		50-106		38		75 75	53 28	19			
Packaging		n/a 200	n/a	6		n/a	75 75		n/a	n/a	n/a	n/a
Vacuum chamber	239 32		92-466		205 27	171	75 75	199	167	n/a	n/a	n/a
Sorting		16	14-54	6		14		27	13	n/a	n/a	n/a
Special cracking	29	9	16-34	6	25	8	75	24	8	n/a	n/a	n/a
b) Area samples	0.2	,	00006	0	2.4	,	,	,	,	,	,	,
Sorting line	83	n/a	80&86	2	24	n/a	n/a	n/a	n/a	n/a	n/a	n/a
d) Compliance monitoring:	210	20	207.242		252	2.4		2.5	2.2	,	,	,
Sorting line in cleaning plant	318	28	287-343	6	273	24	75	265	23	n/a	n/a	n/a
Cello pack. of in-shell walnuts in main bldg.	355	26	326-375	6	304	22	75	296	22	n/a	n/a	n/a
Bulk pack. of in-shell walnuts in main bldg.	243	n/a	242&245	6	208	n/a	75	203	n/a	n/a	n/a	n/a
7. Fumigation and aeration at a brewery facility (T. B.18) a) Applicators												
Entry and reentry to open canisters/cylinders	28.9	n/a	n/a	2	8.3	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Area sample (door to buffer zone)	42	n/a	n/a	$\frac{2}{2}$	12	n/a	n/a	n/a	n/a	n/a	n/a	n/a
b) Aerators		11/ 64	11/ 4	l	12	11/ 4	11/ 44	11/ 4	11, 4	11/ 66	-1/ W	11, 4
Aerators	25	n/a	24&25	2	7	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Area sample (left of entrance door)	173	n/a	n/a	2	49	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Area sample (on applicator's truck)	100	n/a	n/a	2	29	n/a	n/a	n/a	n/a	n/a n/a	n/a	n/a
Area sample (on applicator's truck)	100	11/ d	11/ a		29	11/ a	11/ d	11/ a	11/a	11/ d	11/ a	11/a

Table 11. (continued 3). Acute and non-acute exposures of persons in California to methyl bromide\*.

	Acute	e exposur	re (ppb)	Suba	cute exp.	(ppb)	Subchro	onic exp.	(ppb)	Chronic exp. (ppb)		
Number/	/2	4-hour pe	riod	/7	-day peri	od	/90-	-day peri	od	/365-day period		
Type of application (Data from Table)**	Avg. S7	DEV	Range***	Days	Avg.	STDEV	Days	Avg.	STDEV	Days	Avg. S	TDEV
Appendix C (3). Exposure of residents to MB during commo	odity fumiga	ation (T. (	C.1)									
Low range of exposure days	210	n/a	n/a	3	90	n/a	30	70	n/a	150	86	n/a
High range of exposure days	210	n/a	n/a	6	180	n/a	75	175	n/a	185	106	n/a

Table 12. Acute methyl bromide exposures (95th percentile) of persons at the buffer zone distance following field fumigation.

Field	1 acre					10 acres				20 acres				30 acres					40 acres						
Emission rate*	80	160	200	225	320	80	160	200	225	320	80	160	200	225	320	80	160	200	225	320	80	160	200	225	320
Buffer zone (ft)	110	290	380	420	580	410	1100	1400	1600	2100	610	1600	2000	2300	3100	770	2000	2600	2900	3900	900	2400	3000	3400	4600
MB (ug/m3)	625	677	677	676	672	835	790	769	741	633	874	825	807	802	783	895	827	830	834	849	918	863	860	866	889
MB (ppb)	163	176	176	176	175	217	205	200	193	165	227	215	210	209	204	233	215	216	217	221	239	224	224	225	231

<sup>\*</sup> The emission rate of 80 lbs MB/acre-day was determined for nontarp/shallow/bed fumigation method.

The emission rate of 160 lbs MB/acre-day was determine for tarp/deep/broadcast fumigation method.

The emission rate of 160 lbs MB/acre-day was determine for nontarp/deep/broadcast fumigation method.

The emission rate of 200 lbs MB/acre-day was determine for tarp/shallow/bed fumigation method.

The emission rate of 225 lbs MB/acre-day was determine for drip system-hot gas fumigation method.

 $The\ emission\ rate\ of\ 320\ lbs\ MB/acre-day\ was\ determine\ for\ tarp/shallow/broadcast\ fumigation\ method.$ 

Table 13. Summary: Grouping of methyl bromide acute exposure estimates for workers during fumigations of soil, commodity and brewery facility<sup>a</sup>.

		Methyl bromide	concentration (ppb)	)
Types of fumigation	Replicate	Mean ± STDEV	Range	95 <sup>th</sup> percentile <sup>c</sup>
Soil: Bedded + nonbedded <sup>b</sup>	57	$123 \pm 120$	1 - 518	324
Soil: Bedded <sup>b</sup>	17	$93 \pm 87$	1 - 334	245
Soil: Nonbedded <sup>b</sup>	40	$136 \pm 131$	3 - 515	356
Commodity: Handlers	15	$48 \pm 56$	0.001 - 186	146
Commodity: Other workers	52	$83 \pm 119$	1 - 404	283
Greenhouse: Tarp venters	4	0.01 - 0.02	0.0001 - 0.03	0.05
Greenhouse: Tarp removers	4	$1.0 \pm 0.9$	0.4 - 2.2	3.1
Brewery facility <sup>d</sup>	Exposure re	plicates are not	sufficient for groupi	ing purposes

<sup>&</sup>lt;sup>a</sup> exposure estimates were grouped according to types of fumigations. Data were taken from Table B.19.

Table 14. Methyl bromide concentrations (ppb) based on the Air Resources Board 2000 monitoring studies in Monterey and Santa Cruz and Kern Counties.<sup>a</sup>

		I	Daily	We	ekly	7 or 8-week
	Monitoring	Maximum	95 <sup>th</sup> percentile	Maximum	95 <sup>th</sup> percentile	Mean of
Site <sup>b</sup>	days	24-hour	24-hour	weekly mean	_	weekly means
Mor	nterey and San	ta Cruz Coun	ties (8 monitoring	g weeks, Septem	ber 11 – Novemb	er 3, 2000)
				ppb		
CHU	31	2.41	2.26	1.61	1.63	0.644
LJE	30	24.0	18.5	10.5	11.1	3.79
OAS	31	1.84	1.21	1.01	0.918	0.387
PMS	31	30.8	30.2	15.5	17.1	7.68
SAL	31	7.91	6.17	3.01	3.14	1.29
SES	31	16.4	12.2	8.30	7.45	2.60
		Kern Count	y (7 monitoring w	eeks, July 19 –	September 1, 200	0)
				ppb		
ARB	25	0.996	0.556	0.507	0.507	0.189
CRS	24	14.2	25.4	4.59	5.54	2.16
MET	26	0.224	0.239	0.145	0.163	0.084
MVS	26	0.487	0.262	0.201	0.195	0.092
SHA	26	3.52	3.98	1.77	2.05	0.792
VSD	26	0.347	0.292	0.175	0.181	0.099

Methods and equations used to derive different categories of air concentrations are shown in Appendix D, section 4 - Calculations of MB air concentrations. Data were taken from Table D.1.

b exposure of handlers.

<sup>&</sup>lt;sup>c</sup> arithmetic mean +  $t_{(.95; n-1)}$  x standard deviation (or STDEV).

was not grouped because there are only 1 to 2 replicates for each exposure scenario.

Names of ambient sampling sites (Monterey and Santa Cruz): Chualar School (CHU), La Jolla Elementary School (LJE), Oak Avenue School (OAS), Pajaro Middle School (PMS), MBUAPCD Ambient Monitoring Station, Salinas (SAL), Salsepuedes Elementary School (SES); (Kern): ARB Ambient Monitoring Station (ARB), Cotton Research Station (CRS), Mettler-Fire Station (MET), Mountain View School (MVS), Shafter-Walker Ambient Monitoring Station (SHA), Vineland School District-Sunset School (VSD).

#### **EXPOSURE APPRAISALS**

The exposure appraisal section contains information regarding the quality of exposure studies and the adequacy of submitted reports. This section also briefly describes uncertainty of default factors used in the calculation of exposure estimates. The section also provides some suggestions on how to obtain better exposure estimates for the MB risk assessment.

None of the submitted MB exposure studies met the requirements set forth in Subdivision U (U.S. EPA, 1986b) regarding the number of replicates and locations of the studies, i.e., three locations and five replicates per location for each work task monitored. Many studies provided more than five replicates for each work task, but a majority of the field studies provide replicates ranging from one to three replicates. In most cases, these replicates were from one location. This occurred because DPR had requested expedited development of exposure monitoring data to revise the use permits. Additionally, many studies were not conducted in compliance with GLP standards indicated in 40 CFR 160 (U.S. EPA, 1998).

Reports of the studies were gradually submitted to the Department in the form of interim, internal, or draft reports. Only a few reports were finalized using a format similar to the PR Notice 86-5 (U.S. EPA, 1986c). Currently, many reports are still classified as interim or internal reports; registrants may not accomplish finalizing these reports in the foreseeable future. Nonetheless, these exposure data are shown in this exposure assessment document because registrants were asked by DPR to produce them and the studies were conducted in California.

A field fortification recovery study was not carried out in many of the exposure studies. This may be due to the fact that MB has very high vapor pressure. It is extremely difficult to conduct a field fortification recovery study. Several laboratory recovery studies were performed and the monitoring data were adjusted for recoveries. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). Reports of several studies did not disclose application rates of MB. Authors could not make corrections regarding application rates and field fortification recoveries. Thus, MB concentrations for some of those studies shown in this document could be lower or higher than what they would be in actual work environment.

Duration and frequency of exposure are important factors employed in the calculation of nonacute exposure estimates. DPR realizes that MB registrants can provide data on duration and frequency of exposures because they have close contacts or business relationships with dealers, pest control operators or other users. That was why DPR issued several requests to registrants in November of 1997 for such data. The Department has received some information essential for the estimation of acute and nonacute exposures. DPR has made it clear in those letters that if registrants fail to provide requested data; the Department will derive default factors based upon available information and professional judgment. Authors of this document have conducted data searches, utilized survey results, as well as, consulted with knowledgeable persons on the use of MB. The default factors were established and used in the calculation of subacute and nonacute exposure estimates.

Many exposure data were obtained from studies employing short monitoring periods and then amortized to the 24-hour time-weighted average. These amortized exposure data could overestimate or underestimate the actual exposure.

Exposure estimates shown in this document are generally for specific work tasks and exposure scenarios. In other words, the exposure estimated for forklift drivers in a commodity fumigation or for shovelmen in a soil fumigation was based on a specific time period used to perform those work tasks. It did not take into account the exposure to MB the remainder of the workday if those workers performed other duties. Also, the calculated maximum duration of a workday for acute exposure was based on sources other than current permit conditions. There is a good possibility that the acute exposure was underestimated because workers might work overtime during the peak use season. In contrast, we do not know the degrees of overestimation of exposure when a study was not conducted in compliance with current permit conditions or regulations. Several MB exposure monitoring studies are not included in this document because the fumigation methods used in those studies were not performed in compliance with the permit conditions or regulations. Those studies or parts of those studies were nursery/greenhouse, commodity, potting soil, grain products, dried fruit and tree nuts, and residential reentry studies. It is desirable for the Department to obtain exposure data from studies that are conducted in compliance with the permit conditions or regulations.

MB air concentrations obtained from several studies are grouped based on types of fumigation methods and exposure scenarios. The purpose of grouping of MB concentrations is to show the magnitude of the exposure data and whether a proposed mitigation measure would cover a wide range of exposures. However, a mitigation proposal may not be developed based on grouped MB concentrations if a fumigation method is specific to particular fumigation tools.

Information on some of the variables that is mentioned in this section is intended to be qualitative in nature. It is difficult to judge quantitatively how these variables might affect MOE. For example, if the application rate was not mentioned, the rate could be at the maximum application rate. Hence, this variable would have no effect on exposure or MOE. Furthermore, we do not know if more data on duration and frequency of exposure would affect MOE and to what extent. We do not have sufficient background information to assign numbers to those variables. If we do so, it will cause some uncertainty concerning those assigned numbers.

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Dr. Lori O. Lim, Staff Toxicologist, Toxicology Branch, DPR provided preliminary or summary of the following sections: Physical and chemical properties, regulatory history including U.S. EPA status, animal/human metabolism, and a portion of usage and formulations. Readers may obtain complete information of these sections from the current MB Risk Characterization Document.

#### REFERENCES

- Air Resources Board (ARB). 2000. Ambient air monitoring for methyl bromide and 1,3-dichloropropene in Kern County Summer 2000. Testing Section, Engineering and Certification Branch, Monitoring and Laboratory Division, Air Resources Board. Project No. C00-028. (Final Report).
- ARB. 2001. Ambient air monitoring for methyl bromide and 1,3-dichloropropene in Monterey/Santa Cruz Counties Fall 2000. Testing Section, Engineering and Certification Branch, Monitoring and Laboratory Division, Air Resources Board. Project No. C00-028.
- Air Toxics Limited. 1995. Worker health and safety and ambient air monitoring at Diamond Walnut Growers, Inc. 1992-1994. MB Submission 0265.
- Alexeeff, G. V., and Kilgore, W. W. 1983. Methyl bromide. Residue Reviews 88:101-153.
- Anonymous. 1992. MB monitoring: Farmers rice coop long-term air monitoring possible exposure forklift operators. MB Submission 0156.
- Biermann, H. W., and Barry, T. 1999. Evaluation of charcoal tube and SUMMA canister recoveries for methyl bromide air sampling. Environmental and Pest Management Branch, DPR. EH 99-02.
- Bloomcamp, C. L., Scheffrahn, R. H., and Su, N. Y. 1991. Indoor airborne residues to methyl bromide and sulfuryl fluoride in fumigated houses following aeration. DPN 50223-019, record number 96537.
- Bond, J. A., Dutcher J. S., Medinsky, M. A., Henderson, R. F., and Birnbaum L. S. 1985. Disposition of <sup>14</sup>C-methyl bromide in rats after inhalation. *Toxicol. Appl. Pharmacol.* 78:259-267. (in DPN 123-135, record number 89719).
- Budavari, S., O'Neil, M. J., Smith, A., Heckelman, P. E. (eds.). 1989. *The Merck Index*. Eleventh edition. Merck & Co., Inc., Rahway, NJ. 1606 pp.
- California Department of Food and Agriculture (CDFA). 1984a. Determination of methyl bromide residues in strawberries after a commercial fumigation. DPN 123-089.
- CDFA. 1984b. Methyl bromide residues in wheat and flour during fumigation, storage, clearing, and milling in a commercial milling facility. DPN 123-089.
- California Code of Regulations (CCR). 2000. Chapter 1. Pesticide Regulatory Program, Subchapter 4, Restricted Materials, Article 4. Use Requirements, Section 6454 Chloropicrin and Methyl Bromide Structural Fumigation.
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- CCR. 2001. Chapter 3. Pest Control Operations, Subchapter 3. Pesticide Worker Safety, Article 4. Fumigation, Section 6784. Field Fumigation.
- Danse, L. H. J. C., van Velsen, F. L., and van der Heijden, C. A. 1984. Methyl bromide: Carcinogenic effects in the rat forestomach. *Toxicol. Appl. Pharmacol.* 72:262-271. (in DPN 123-043, record number 913094).
- Deschamps, F. J., and Turpin, J. C. 1996. Methyl bromide intoxication during grain store fumigation. *Occup. Med.* 46: 89-90.
- Donahue, J. M. 1997. DPR letters dated November 12. (Letters were sent to six MB registrants requesting data on duration and frequency of exposure). WH&S, DPR.
- DPR. 1999a. Summary of pesticide use report data in 1996: Indexed by chemical. DPR.
- DPR. 1999b. Summary of pesticide use report data in 1997: Indexed by chemical. DPR.
- DPR. 2000a. Summary of pesticide use report data in 1998: Indexed by chemical. DPR.
- DPR. 2000b. Summary of pesticide use report data in 1999: Indexed by chemical. DPR.
- DPR. 2001. Guidance Manual: Methyl bromide (in combination with chlroropicrin). Field soil fumigation. DPR (Draft).
- Fairall, R. J., and Scudamore, K. A. 1980. Determination of residual methyl bromide in fumigated commodities using derivative gas chromatography. *Analyst* 105:251-256.
- Federal Register. 1991. Code of Federal Regulations, 40 Part 180.3 (c)(2). Office of the Federal Register, National Archives and Records Administration. U.S. Government Printing Office, Washington, D.C.
- Gibbons, D. 1992. A letter dated May 11 to John Sansone of SCC Products regarding the MB data from a joint structural fumigation study in Los Angeles. WH&S, DPR. HSM-92002.
- Gibbons, D. B. 1994. Department of Pesticide Regulation monitoring of methyl bromide fumigation at Anheuser-Busch Brewery. A memorandum dated December 27 to Dane Starling of Anheuser-Busch, Inc. HSM-94002.
- Gibbons, D. B. 1995. Compliance monitoring at Diamond Walnut. A memorandum dated November 2 to Chuck Andrews of the Pesticide Enforcement Branch, DPR. HSM-95001.
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Gibbons, D. B., Fong, H. R., Segawa, R., Powell, S., and Ross, J. 1996a. Methyl bromide concentrations in air near fumigated single-family houses. WH&S, DPR. HS-1717. (Final Report).
- Gibbons, D. B., Fong, H. R., Segawa, R., Powell, S., and Ross, J. 1996b. Methyl bromide concentrations in air downwind during aeration of fumigated single-family houses. WH&S, DPR. HS-1713. (Final Report).
- Harris, M. C., Harvey, J. M., and Fouse, D.C. 1983. Penetration and retention of methyl bromide in packaged table grapes. *American Journal of Enology and Viticulture* 35:5-8.
- Hartsell, P. L., Nelson, H. P., and Vail, P. V. 1984a. Walnut research reports. DPN 123-089.
- Hartsell, P. L., Nelson, H. P., and Stanley, W. L. 1984b. Methyl bromide fumigation of almonds and almond products. DPN 123-089.
- Hartsell, P. L., Nelson, H. D., Tebbets, J. C., and Vail, P. V. 1986. Methyl bromide fumigation treatments for pistachio nuts to decrease residues and control navel orangeworm, <u>Amyelois transitellia</u> (Lepidoptera: Pyralidae). *J. Econ. Entomol.* 79:1299-1302.
- Hartsell, P. L., Obenauf, G. L., Gunnerson, R. E., and Mosebar, F. A. 1992. Methyl bromide residue studies on dried fruit and nuts. Prune, Raisin and Walnut Marketing Board. MB Submission 0078.
- Haskell, D. 1998a. Methyl bromide fumigation with various commodities. A memorandum dated May 11 to Thomas Thongsinthusak. WH&S, DPR. HSM-98003.
- Haskell, D. 1998b. Response to DPR request for additional information regarding frequency and duration of methyl bromide fumigations. A memorandum dated August 24 to Thomas Thongsinthusak. WH&S, DPR. HSM-98006.
- Helliker, P. E. 1999. Status of methyl bromide permit conditions. A letter to interested parties. DPR. August 31.
- Hezemans-Boer, M., Toonstra, J., Meulenbelt, J., Zwaveling, J. H., Sangster, B., and van Vloten W. A. 1988. Skin lesions due to exposure to methyl bromide. *Arch. Dermatol.* 124: 917-921.
- Hosoda, E. 1992. Methyl bromide monitoring. The Grain Product Group. Cal Ag-Industrial Supply, Inc. (Final Report).
- Ingram, F. R. 1951. Methyl bromide fumigation and control in the date-packing industry. *Arch. Ind. Hyg. Occup. Med.* 4:193-198.
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Jaskot, R. H., Grose, E. C., Most, B. M., Menache, M. G., Williams, T. B., and Roycroft, J. J. 1988. The distribution and toxicological effects of inhaled methyl bromide in the rat. *J. Am. Coll. Toxicol.* 7:631-642. (in DPN 123-135, record number 89717).
- Johnson, B. 2001. Determination of frequency distributions of required buffer zones for daily concentrations of methyl bromide. Environmental Monitoring and Hazards Assessment Program, DPR. EH00-10 (Draft). November.
- Johnstone, R. T. 1944. Methyl bromide intoxication. *Industr. Med.* 14:495-497.
- Jordi, A. U. 1953. Absorption of methyl bromide through the intact skin: A report of one fatal and two nonfatal cases. *Airspace Med. J.* 24:536-539.
- King, J. R., Benschoter, C. A., and Burditt, A. K. 1981. Residues of methyl bromide in fumigated grapefruit determined by a rapid, headspace assay. DPN 123-116.
- Le Goupil, M. 1932. Les proprieties insecticide du bromure de methyl. *Rev. Pathol. Veg. Entomol. Agr. Fr.* 19:169.
- Longley, E. O., and Jones, A. T. 1965. Methyl bromide poisoning in man. *Ind. Med. Surg.* 34:499-502.
- MacDonald, A. C., Monro, I. C, and Scott, G. I. 1950. Fatal case of poisoning due to inhalation of methyl bromide. *Brit. Med. J.* 2:441-442.
- Malone, B. 1970. Isolation of methyl bromide from food raw materials for gas chromatographic quantitation. *J. AOAC* 53.
- McDougal, J. N., Jepson, G. W., Clewell III, H. J., and Andersen, M. E. 1985. Dermal absorption of dihalomethane vapors. *Toxicol. Appl. Pharmacol.* 79: 150-158.
- McDougal, J. N., Jepson, G. W., Clewell III, H. J., Gargas, M. L., and Andersen, M. E. 1990. Dermal absorption of organic chemical vapors in rats and humans. *Fund. Appl. Toxicol.* 14: 299-308.
- Medinsky, M. A., Bond, J. A., Dutcher, J. S., and Birnbaum, L. S. 1984. Disposition of [<sup>14</sup>C] methyl bromide in Fischer-344 rats after oral or intraperitoneal administration. *Toxicology* 32:187-196. (in DPN 123-135, record number 89720).
- Medinsky, M. A., Dutcher, J. S., Bond, J. A., Henderson, R. F., Mauderly, J. L., Snipes, M. B., Mewhinney, J. A., Cheng, Y. S., and Birnbaum, L. S. 1985. Uptake and excretion of [<sup>14</sup>C] methyl bromide as influenced by exposure concentration. *Toxicol. Appl. Pharmacol.* 78:215-225. (in DPN 123-135, record number 89718).
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Mehler, L. 2001. Summary: Illnesses associated with exposure to methyl bromide alone and in combination as reported by physicians in California from 1991 to 1999. Pesticide Illness Surveillance Program, WH&S, DPR.
- Meister, R. T. (ed.). 1995. *Farm Chemicals Handbook*. Meister Publishing Company, Willoughby, OH.
- Mezel, P., Bourret, J., and Roche, L. 1948. Poisoning of the whole family of five persons following upon the use of methyl bromide to disinfect a dwelling. Three deaths. *Ind. Hyg. Toxicol.* 23:527.
- National Research Council (NRC). 2000. Methyl Bromide Risk Characterization in California. Subcommittee for the Review of the Risk Assessment of Methyl Bromide. National Academy Press, Washington, DC.
- Nelson, L. 1992. Methyl bromide preliminary risk characterization. A memo dated February 11 to Jim Wells, DPR.
- Nelson, H. D., Hartsell, P. L., Armstrong, J. W., Down, L. L., and Lee, R. 1975. Annual Report, Almond Board of California-Project 75-I. MB Submission 0077.
- NIOSH. 1987. NIOSH Respirator Decision Logic. U.S. Department and Human Services, Public Health Services, Center for Disease Control, National Institute for Occupational Safety and Health. May.
- Obenauf, G. L. 1992. Prune, Raisin and Walnut Marketing Boards. MB Submission 0079.
- Powell, S. 2001. Exposure to methyl bromide based on ARB 2000 monitoring in Monterey/Santa Cruz and Kern Counties. A memorandum to Joe Frank dated February 9. WH&S, DPR. HSM-01004.
- Raabe, O. G. (University of California, Davis). 1986. Inhalation uptake of selected chemical vapors at trace levels. The Biological Effects Research Section, California Air Resources Board (CARB), Sacramento, CA. CARB Contract No. A3-132-33.
- Raabe, O. G. (University of California, Davis). 1988. Retention and metabolism of toxics. inhalation uptake of xenobiotic vapors by people. The Biological Effects Research Section, California Air Resources Board, Sacramento, CA. CARB Contract No. A5-155-33.
- Radian Corporation. 1992. Determination of methyl bromide exposure during dried fruit and tree nut fumigation practices, volumes I & II. MB Submission 0200. (Final Report).
- Rathus, E. M., and Randy, P. J. 1961. Methyl bromide poisoning. Brit. J. Ind.. Med. 18:53-57.
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Reuzel, P. G. J., Kuper, C. F., Dreef-van der Meulen, H. C., and Hollanders, V. M. H. (Civo Institutes TNO). 1987. Chronic (29-month) inhalation toxicity and carcinogenicity study of methyl bromide in rats. DPN 123-084, record number 59184; DPN 123-147, record number 116337; DPN 123-148, record number 120402; DPN 123-148, record number 120406; and DPN 123-166, record number 133417.
- Reuzel, R. G. J., Dreef-van der Meulen, H. C., Hollanders, V. M. H., Kuper, C. F., Feron, V. J., and van der Heijden, C. A. 1991. Chronic inhalation toxicity and carcinogenicity study of methyl bromide in Wistar rats. *Food Chem. Toxicol.* 29:31-39.
- Richmond, D. 1997. Priority investigations as a result of evacuation after the use of methyl bromide in California from 1982 to 1995 (Personal communication). Pesticide Illness Surveillance Program, WH&S, DPR.
- Riihimaki, V., and Pfaffli, P. 1978. Percutaneous absorption of solvent vapors in man. *Scand. J. Work Environ. & Health* 4: 73-85.
- Ross, J. H., and Gibbons, D. B. 1992. Cal/EPA, Department of Pesticide Regulation methodology for measuring methyl bromide exposure to application personnel and other potentially exposed workers (6/12). Cal/EPA, Department of Pesticide Regulation. HSM-92001.
- Sanders, J. S. 1998. Definition of exposure constituting chronic and subchronic. A memorandum dated March 10 to G. Patterson of the Medical Toxicology Branch, DPR. HSM-98009.
- Sanders, J. S., and Andrews, C. M. 1998. Installation of irrigation pipe during soil fumigation. A letter dated July 7 to County Agricultural Commissioners. DPR. CAC letter WHS 98-04.
- Sanders, J. S. 2000. Recommendation for 1,3-dichloropropene and methyl bromide monitoring for the toxic air contaminant program. A memorandum to George Lew of the Air Resources Board dated June 6. Environmental Monitoring and Pest Management Branch. DPR.
- Sansone, J. S. 1998. Typical methyl bromide structural fumigation rates in California. Phone conversations with Dennis Gibbons and Tom Thongsinthusak on June 5.
- Sell, C. R., Klag, N. G., and Burditt, A. K. 1987. Methyl bromide residues in fresh cherries: Effects of parameters of fumigation. *Pesticide Science* 23:41-49.
- Siemer & Associates, Inc. 1992a. Shallow-shank tarp method of methyl bromide fumigation worker exposure. Alliance of the Methyl Bromide Industry (AMBI). MB Submission 0239 A-D (Final Report No. SM924096A-D).
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Siemer & Associates, Inc. 1992b. Nontarp deep injection for measurement of methyl bromide exposure to the applicator, applicator assistant and cultipacker tractor driver (Interim Report No. SM924096B).
- Siemer & Associates, Inc. 1992c. AMBI: Shallow shank-tarped bed fumigation assessment (Interim Report No. SM924096C, M).
- Siemer & Associates, Inc. 1992d. Nursery Panel methyl bromide worker exposure assessment from potting soil fumigation (Interim Report No. SM924099B).
- Siemer & Associates, Inc. 1992e. Nursery Panel Methyl Bromide Task Force: Worker exposure and drift assessment (Interim Report No. SM924099A1).
- Siemer & Associates, Inc. 1993a. Deep shank bed fumigation using mitigation measures to limit worker exposure (Interim Report No. SM934104-1.2).
- Siemer & Associates, Inc. 1993b. Deep shank, nontarped fumigation-mitigation of methyl bromide worker exposure and offsite drift (Interim Report No. SM934104.1-2, Report No. SM934104.2-1, vol. 1-2).
- Siemer & Associates, Inc. 1993c. Tarped-bed fumigation mitigation of methyl bromide worker exposure (Interim Report No. SM934104.1M).
- Siemer & Associates, Inc. 1994. Tarp-bed fumigation for measurement of methyl bromide exposure, to the applicator, applicator assistant, shovelman, irrigation pipelayers and pipe drive positions (Interim Report No. SM934110). MB Submission 0266 B-C.
- Sinclair, W. B., and Lindgren, D. 1952. Effect of load in fumatorium on sorption of fumigants. Paper 728. University of California Citrus Experimental Station, Riverside, California.
- Singh, G., Rippon, L. E., and Gilbert, W. S. 1982. Methyl bromide and organic bromide residues in avocados after fumigation and storage. *Aust. J. Exp. Agric. Anim. Husb.* 22:343-347.
- Soderstrom, E. L., Brandl, D. G., Hartsell, P. L., and Mackey, B. 1991. Fumigants as treatments for harvested citrus fruits infested with <u>Asynonychus godmani</u> (Coleoptera: Curculionidae). *J. Econ. Entomol.* 84:936-941.
- Soil Chemicals Corp. 1980. Application and fumigation data for 24-c registration of methyl bromide for structural fumigation. DPN 123-025, record number 29764.
- Stegmiller, F. R., and Lee, H. 1992. Inhalation exposure of applicators and handlers of methyl bromide treated fresh cherries for export 1992. Bioentech Incorporated and Bolsa Research Associates, Inc. (Interim Report).
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Tebbets, J. S., Hartsell, P. L., Nelson, H. D., and Tebbets, J. C. 1983. Methyl bromide fumigation of tree fruits for control of the Mediterranean Fruit Fly: Concentration, sorption and residues. *J. Agric. Food Chem.* March:247-249.
- TriCal, Inc. 1987. Response/California Notice 87-5: Risk assessment/methyl bromide. DPN 123-099, record numbers 64748 to 64753.
- TriCal, Inc. 1990. Worker exposure data-12" tarpless. DPN 123-119, record numbers 95086 and 95087 (Also, DPN 123-120)
- TriCal, Inc. 1993a. Tarp removal worker exposure. Vol. 1-2 (TC 211).
- TriCal, Inc. 1993b. New high barrier film evaluation studies (TC233.1, TC233.2, TC233.3).
- U.S. EPA. 1986a. Guidance for the registration of pesticide products containing methyl bromide as the active ingredient. Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1986b. Pesticide Assessment Guidelines. Subdivision U: Applicator Exposure Monitoring. OPP/HED, Washington, D.C.
- U.S. EPA. 1986c. PR Notice 86-5. Notice to producers, formulators, distributors and registrants. Standard format for data submitted under the FIFRA and certain provision of the FFDCA. U.S. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1992. Bromomethane, 4/6/92, Integrated Risk Information System (IRIS), U.S. Environmental Protection Agency, Washington, D.C.
- U.S. EPA. 1998. Good Laboratory Practice Standard. 40 CFR Part 160.
- von Oettingen, W. F. 1946. The toxicity and potential dangers of methyl bromide with special reference to its use in the chemical industry, in fire extinguishers, and in fumigation. *NIH Bulletin No. 185*, pp. 1-41.
- Watrous, R. M. 1942. Methyl bromide local and mild systemic effects. *Industr. Med.* 11:575-579.
- Watson, R. T., Albritton, D. L., Andersen, S. O., and Lee-Bapty, S. 1992. Synthesis report of the methyl bromide interim scientific assessment and methyl bromide interim technology and economic assessment. Montreal Protocol Assessment Supplement. Requested by United Nations Environment Programme on behalf of the Contracting Parties to the Montreal Protocol. June 25.
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

- Wieczorek, H. 1985. Evaluation of low exposure to styrene. II. Dermal absorption of styrene vapors in humans under experimental conditions. *Int. Arch. Environ. Health.* 57: 71-75.
- Zwaveling, J. H., de Kort, W. L. A. M., Meulenbelt, J., Hezemans-Boer, M., van Vloten, W. A., and Sanster, B. 1987. Exposure of the skin to methyl bromide: A study of six cases occupationally exposed to high concentrations during fumigation. *Human Toxicol*. 6:491-495.
- (DPN is the Data Package Number as assigned by the DPR Pesticide Registration Branch, which is unique for DPR; MB Submission means a report that was not assigned a DPN)

 $\label{eq:Appendix A} \textbf{Appendix A} \\ \textbf{Duration and frequency of acute and nonacute exposures for workers and residents}^a$ 

		Adjustment rate (ref) <sup>d</sup>	Hours/wo	orkday (ref.) <sup>e</sup>	Workdays (ref.)		
Section <sup>b</sup>	Work task <sup>c</sup>	(lb. MB/A)	Acute	Subc-chronic	/7 days	/90 days	/365 days
a	Shallow shank-tarped soil fumigation (broadcast)						
	Applicators (used Noble Plow shanks, 10-12")	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Co-pilots	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Shovelmen: Employed by growers	400 (1)	5.8 (7)	n/a-n/a (6)	3 (8)	n/a (6)	n/a (6)
	Tarpaulin removers: Employed by private companies	400 (1)	6 (6)	6-n/a (6)	5 (8)	55 (8)	n/a (6)
	Tarpaulin removers: Employed by growers	400 (1)	2 (6)	n/a-n/a (6)	2 (8)	n/a (6)	n/a (6)
b	Nontarp deep shank injection fumigation (broadcast)						
	Applicators (used improved shank, 20-24")	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Co-pilots: Employed by application rigs	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Cultipacker tractor drivers: Employed by growers	400 (1)	5.8 (7)	n/a-n/a (6)	6 (8)	n/a (6)	n/a (6)
c	Nontarp deep shank injection fumigation (Traver, etc., CA)						
	Applicators (used forward curving inj. shank, cl. scraper, 24")	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Disc drivers: Employed by PCOs	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Cultipacker tractor drivers: Employed by growers	400 (1)	5.8 (7)	n/a-n/a (6)	6 (7)	n/a (6)	n/a (6)
	Supervisor: Employed by PCOs	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
d	Nontarp deep shank injection fumigation (Helm, CA)						
	Applicators (used forward curving shank, 24")	400 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Cultipackers: Employed by growers	400 (1)	5.8 (7)	n/a-n/a (6)	6 (7)	n/a (6)	n/a (6)
e	Shallow shank-tarped bed fumigation						
	Applicators (used modified shanks, 6-8")	250 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Co-pilots	250 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
f	Tarped-bed fumigation: Mitigation of exposure						
	Applicators (used Kennco Combi Superbedder, 14")	250 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Co-pilots	250 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Drip tape layers: Employed by growers	250 (1)	5.8 (7)	n/a-n/a (6)	3 (8)	n/a (6)	n/a (6)

<sup>&</sup>lt;sup>a</sup> nonacute exposures include subacute, subchronic and chronic exposures.

b section corresponds to that in Appendices B and C.

<sup>&</sup>lt;sup>c</sup> PCO = Pest control operator; BH = high barrier; VHB = very high barrier; PE = polyethylene.

an application rate that was used to adjust MB concentrations obtained from a study using a different application rate.

e exposure times as indicated were used for the calculation of daily acute, subchronic (subchr.) and chronic (chr.) exposures (Tables B.1-B.18, C.1). n/a = not applicable.

# Appendix A (Continued 1)

		Adjustment rate (ref) <sup>d</sup>	Hours/wo	rkday (ref.) <sup>e</sup>	7	Workdays (re	f.)
Section <sup>b</sup>	Work task <sup>c</sup>	(lb. MB/A)	Acute	Subc-chronic	/7 days	/90 days	/365 days
g	Shallow shank, tarped bed fumigation						
	Applicators (used sweptback shank, 8")	250 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Co-pilots	250 (1)	5.8 (7)	5.8-n/a (7)	6 (7)	40 (7)	n/a (7)
	Shovelmen: Employed by growers	250 (1)	5.8 (7)	n/a-n/a (6)	3 (8)	n/a (6)	n/a (6)
h	Tarp removers (shallow shank, broadcast, HB, 10-12")						
	Cutters: Growers	400 (1)	2 (6)	n/a-n/a (6)	2 (8)	n/a (8)	n/a (6)
	Cutter: Employed by independent companies	400 (1)	6 (6)	6-n/a (6)	5 (8)	30 (8)	n/a (6)
	Pullers: Employed by growers	400 (1)	2 (6)	n/a-n/a (6)	2 (8)	n/a (8)	n/a (6)
	Puller: Employed by independent companies	400 (1)	6 (6)	6-n/a (6)	5 (8)	30 (8)	n/a (6)
i	Tarp cutters and removers						
	Cutters (Fum. Shallow, broadcast, VHB, Noble Plow shank, 10")	400 (1)	2 (6)	n/a-n/a (6)	5 (8)	n/a (6)	n/a (6)
	Removers: Employed by growers	400 (1)	2 (6)	n/a-n/a (6)	5 (8)	n/a (6)	n/a (6)
	Cutters and removers: Employed by independent companies	400 (1)	6 (6)	6-n/a (6)	5 (8)	30 (8)	n/a (6)
2.a	Nursery potting soil fumigation						
	Applicators (used perforated plastic hoses, 6-mil PE)	$0.6/yd^3(3)$	1 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Applicator assistants	$0.6/yd^3(3)$	1 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Tarp removers	$0.6/yd^3(3)$	1 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Tractor drivers	$0.6/yd^3(3)$	1 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Truck drivers	$0.6/yd^3(3)$	1 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Potters	$0.6/\text{yd}^3(3)$	3 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
2.b	Greenhouse soil fumigation						
	Applicators (used perforated plastic hoses, 1 mil HDT)	450 (2)	2 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Tarp venters	450 (2)	1 (6)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
	Tarp removers	450 (2)	1 (7)	n/a-n/a (6)	1 (6)	n/a (6)	n/a (6)
							<u> </u>
3	Fumigation of grain products (chambers, vans, etc.)	2					
	Applicators (6 mil PE, if used)	6/1,000 ft <sup>3</sup> (4)	6 (6)	6.5-5 (6)	5 (6)	45 (6)	180 (6)
	Aerators	6/1,000 ft <sup>3</sup> (4)	6 (6)	6.5-5 (6)	5 (6)	45 (6)	180 (6)
	Forklift drivers	$6/1,000 \text{ ft}^3(4)$	1 (6)	0.5-0.5 (6)	5 (6)	45 (6)	180 (6)
	Rice processing workers (Warehouse)	$6/1,000 \text{ ft}^3(4)$	6 (8)	n/a-n/a (6)	5 (8)	n/a (6)	n/a (6)

<sup>&</sup>lt;sup>a</sup> nonacute exposures include subacute, subchronic and chronic exposures.

b section corresponds to that in Appendices B and C.

<sup>&</sup>lt;sup>c</sup> PCO = Pest control operator; BH = high barrier; VHB = very high barrier; PE = polyethylene.

an application rate that was used to adjust MB concentrations obtained from a study using a different application rate.

e exposure times as indicated were used for the calculation of daily acute, subchronic (subchr.) and chronic (chr.) exposures (Tables B.1-B.18, C.1). n/a = not applicable.

# **Appendix A (Continued 2)**

		Adjustment rate (ref) <sup>d</sup>	Hours/w	orkday (ref.) <sup>e</sup>	7	Workdays (re	f.)
Section <sup>b</sup>	Work task <sup>c</sup>	(lb. MB/A)	Acute	Subc-chronic	/7 days	/90 days	/365 days
4	Fumigation of dried fruit & tree nut products						
	1. Sea van						
	Fumigators	1.5/1,000 ft <sup>3</sup> (4)	1 (6)	n/a-n/a (6)	2 (6)	n/a 6)	n/a (6)
	Fumigator observers	$1.5/1,000 \text{ ft}^3(4)$	1 (6)	n/a-n/a (6)	2 (6)	n/a (6)	n/a (6)
	Aerators	$1.5/1,000 \text{ ft}^3(4)$	1 (8)	n/a-n/a (8)	2 (6)	n/a (8)	n/a (8)
	Area sampling (15-foot downwind)	$1.5/1,000 \text{ ft}^3(4)$	1 (8)	n/a-n/a (8)	2 (8)	n/a (8)	n/a (8)
	2. Chamber (dried prunes)						
	Forklift operators	$1.5/1,000 \text{ ft}^3(4)$	0.5 (7)	n/a-n/a (6)	3 (7)	n/a (7)	n/a (7)
	Fumigators	$1.5/1,000 \text{ ft}^3(4)$	0.5 (7)	n/a-n/a (6)	3 (7)	n/a (7)	n/a (7)
	1-m from door	$1.5/1,000 \text{ ft}^3(4)$	0.5 (7)	n/a-n/a (6)	3 (7)	n/a (7)	n/a (7)
	2 & 15 m from chamber	$1.5/1,000 \text{ ft}^3(4)$	0.5 (7)	n/a-n/a (6)	3 (7)	n/a (7)	n/a (7)
	Leak check, side seal	1.5/1,000 ft <sup>3</sup> (4)	0.5 (7)	n/a-n/a (6)	3 (7)	n/a (7)	n/a (7)
	3. Big chamber fumigation (raisins)						
	Primary fumigators	$1.5/1,000 \text{ ft}^3(4)$	3 (6)	2.5-2.5 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Secondary fumigators	$1.5/1,000 \text{ ft}^3(4)$	3.5 (6)	2.5-2.5 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Aerators	$1.5/1,000 \text{ ft}^3(4)$	3 (6)	2.5-2.5 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Forklift drivers	$1.5/1,000 \text{ ft}^3(4)$	2.5 (6)	2-2 (6)	5 (6)	60 (6) <sup>f</sup>	20&170g(6)
	Catchall operators	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170g(6)
	Hopper operators	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Capper dumpers	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Inspectors	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Moisture checkers	1.5/1,000 ft <sup>3</sup> (4)	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Stem pickers	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Packers	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	5 (6)	60 (6) <sup>f</sup>	20&170 <sup>g</sup> (6)
	Shed-green forklift	$1.5/1,000 \text{ ft}^3(4)$	2.5 (6)	2-2 (6)	5 (6)	60 (6) <sup>f</sup>	20&170g(6)
	Shed-blue tractor	$1.5/1,000 \text{ ft}^3(4)$	2.5 (6)	2-2 (6)	5 (7)	60 (6) <sup>f</sup>	20&170g(6)
	Aeration-shed 604-606	$1.5/1,000 \text{ ft}^3(4)$	3 (8)	2.5-2.5 (8)	5 (8)	60 (8)	20&170g(6)
	Capper area	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (6)	5 (6)	60 (6)	20&170 <sup>g</sup> (6)
	Hopper area	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (6)	5 (6)	60 (6)	20&170 <sup>g</sup> (6)

<sup>&</sup>lt;sup>a</sup> nonacute exposures include subacute, subchronic and chronic exposures.

b section corresponds to that in Appendices B and C.

<sup>&</sup>lt;sup>c</sup> PCO = Pest control operator; BH = high barrier; VHB = very high barrier; PE = polyethylene.

an application rate that was used to adjust MB concentrations obtained from a study using a different application rate.

e exposure times as indicated were used for the calculation of daily acute, subchronic (subchr.) and chronic (chr.) exposures (Tables B.1-B.18, C.1). n/a = not applicable.

average value from three large commodity fumigation facilities.

each average value represents three small chambers (30, 20, and 20 days/year) and three large chambers (90, 200, and 220 days/year) for commodity fumigation facilities. The higher value was used for the estimation of MB exposure in this document.

# **Appendix A (Continued 3)**

		Adjustment rate (ref) <sup>d</sup>	Hours/wo	orkday (ref.) <sup>e</sup>	V	Workdays (ref.)	
Section <sup>b</sup>	Work task <sup>c</sup>	(lb. MB/A)	Acute	Subc-chronic	/7 days	/90 days	/365 days
	3. Big chamber fumigation (raisins) (continued)						
	Catchoff area	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (6)	5 (6)	60 (6)	20&170 <sup>g</sup> (6)
	Side hopper area	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (6)	5 (6)	60 (6)	20&170g(6)
	Stem picker area	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (6)	5 (6)	60 (6)	20&170g(6)
	Filler area, E-line	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (6)	5 (6)	60 (6)	20&170 <sup>g</sup> (6)
	4. Chamber (raisins)						
	Fumigators	$1.5/1,000 \text{ ft}^3(4)$	1.5 (6)	1.5-1 (6)	6 (6)	63 (6)	150 (6)
	Aerators	$1.5/1,000 \text{ ft}^3(4)$	1.5 (6)	1.5-1 (6)	6 (6)	63 (6)	150 (6)
	Forklift drivers	$1.5/1,000 \text{ ft}^3(4)$	1 (6)	1-0.4 (6)	6 (6)	63 (6)	150 (6)
	Hopper operators	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	6 (6)	63 (6)	150 (6)
	Stem picker	$1.5/1,000 \text{ ft}^3(4)$	8 (6)	8-8 (6)	6 (6)	63 (6)	150 (6)
	Fumigation area, cage	$1.5/1,000 \text{ ft}^3(4)$	1.5 (8)	1.5-1 (8)	6 (8)	63 (8)	150 (6)
	Leak check	$1.5/1,000 \text{ ft}^3(4)$	0.5 (8)	n/a-n/a (8)	n/a (8)	n/a (8)	n/a (8)
	Aeration chambers	$1.5/1,000 \text{ ft}^3(4)$	1.5 (6)	1.5-1 (6)	6 (6)	63 (6)	150 (6)
	Clearing chamber	$1.5/1,000 \text{ ft}^3(4)$	1.5 (8)	1.5-1 (8)	6 (8)	63 (8)	150 (8)
	Hopper area	$1.5/1,000 \text{ ft}^3(4)$	8 (8)	8-8 (8)	6 (8)	63 (8)	150 (8)
	5. Fumigation of noncertified chambers (nuts)						
	Fumigators	$3.5/1,000 \text{ ft}^3(4)$	5.5 (6)	4-2.5 (6)	6 (6)	70 (6)	185 (6)
	Cleaning fumigator	$3.5/1,000 \text{ ft}^3(4)$	5.5 (8)	4-2.5 (8)	6 (8)	70 (8)	185 (8)
	Cracking, sorting, cleaning, packing	$3.5/1,000 \text{ ft}^3(4)$	8 (6)	8-n/a (6)	6 (6)	70 (6)	n/a (6)
	Bulk casing worker	$3.5/1,000 \text{ ft}^3(4)$	8 (8)	8-n/a (8)	6 (8)	70 (8)	n/a (8)
	Hopper operator	$3.5/1,000 \text{ ft}^3(4)$	8 (8)	8-n/a (8)	6 (8)	70 (8)	n/a (8)
	Area sampling: Fumigatorium	$3.5/1,000 \text{ ft}^3(4)$	5.5 (8)	4-2.5 (8)	6 (8)	70 (8)	185 (8)
	Area sampling: Sorting, cracking,	3.5/1,000 ft <sup>3</sup> (4)	8 (8)	8-n/a (8)	6 (8)	70 (8)	n/a (8)
	Vacuum chamber area	3.5/1,000 ft <sup>3</sup> (4)	8 (8)	8-n/a (8)	6 (8)	70 (8)	n/a (8)
	Cleaning building fumigator	3.5/1,000 ft <sup>3</sup> (4)	4 (8)	4-2.5 (8)	6 (8)	70 (8)	185 (8)
	6. Sea van aeration	2					
	Upwind and downwind areas	$3.5/1,000 \text{ ft}^3(4)$	0.5 (8)	0.5-n/a (8)	6 (8)	70 (8)	n/a (8)

<sup>&</sup>lt;sup>a</sup> nonacute exposures include subacute, subchronic and chronic exposures.

b section corresponds to that in Appendices B and C.

<sup>&</sup>lt;sup>c</sup> PCO = Pest control operator; BH = high barrier; VHB = very high barrier; PE = polyethylene.

an application rate that was used to adjust MB concentrations obtained from a study using a different application rate.

e exposure times as indicated were used for the calculation of daily acute, subchronic (subchr.) and chronic (chr.) exposures (Tables B.1-B.18, C.1). n/a = not applicable.

f average value from three large commodity fumigation facilities.

each average value represents three small chambers (30, 20, and 20 days/year) and three large chambers (90, 200, and 220 days/year) for commodity fumigation facilities. The higher value was used for the estimation of MB exposure in this document.

# **Appendix A (Continued 4)**

		Adjustment rate (ref) <sup>d</sup>	Hours/wo	orkday (ref.) <sup>e</sup>	Workdays (ref.)		
Section <sup>b</sup>	Work task <sup>c</sup>	(lb. MB/A)	Acute	Subc-chronic	/7 days	/90 days	/365 days
5	Fumigation of cherries for export				-chronic /7 days /90 days  -chronic /90 days  -chronic /90 days  -chronic /90 days  -chronic /90 days		
	Control room: Start-up	$5/1,000 \text{ ft}^3(4)$	1 (6)	n/a-n/a (6)		n/a (6)	
	Control room: Left overnight	5/1,000 ft <sup>3</sup> (4)	1 (6)	n/a-n/a (6)	5 (6)	n/a (6)	n/a (6)
	Fumigators	$5/1,000 \text{ ft}^3(4)$	1 (6)	n/a-n/a (6)	5 (6)	n/a (6)	n/a (6)
	Closing-up, opening-up	$5/1,000 \text{ ft}^3(4)$	1 (6)	n/a-n/a (6)	5 (6)	n/a (6)	n/a (6)
	Forklift drivers	$5/1,000 \text{ ft}^3(4)$	0.75 (6)	n/a-n/a (6)	5 (6)	n/a (6)	n/a (6)
	Sorters	$5/1,000 \text{ ft}^3(4)$	8 6)	n/a-n/a (6)		n/a (6)	n/a (6)
	Dump station	5/1,000 ft <sup>3</sup> (4)	8 (6)	n/a-n/a (6)	5 (6)	n/a (6)	n/a (6)
6	Fumigation at a walnut processing facility	Study rate-not known					
	Meats pool, bulk packaging, cleaning plant, cracking	no adjustment	8 (6)	8-n/a (6)	6 (6)	75 (6)	n/a (6)
	Warehouse workers (storage area)	no adjustment	8 (6)	8-8 (6)	6 (6)	75 (6)	180 (6)
	Warehouse aisle	no adjustment	8 (6)	8-n/a (6)	6 (6)	75 (6)	n/a (6)
	Sorting line	no adjustment	8 (6)	8-n/a (6)	6 (6)	75 (6)	n/a (6)
	Fumigatorium	no adjustment	5.5 (6)	4-2.5 (6)	6 (6)	75 (6)	180 (6)
	Cleaning plant	no adjustment	8 (6)	8-n/a (6)	6 (6)	75 (6)	n/a (6)
	Vacuum chamber	no adjustment	8 (6)	8-n/a (6)	6 (6)	75 (6)	n/a (6)
	Nonwork areas (vicinity of fumigation chambers, fence line,	no adjustment	0.5 (8)	n/a-n/a (8)	2 (8)	n/a (8)	n/a (8)
	alleyway, lamp posts, etc.)						
	Compliance monitoring study:						
	Foreman's desk top	Study rate-not known	8	8-8 (8)			180 (8)
	Foreman's desk, phone box shelf	no adjustment	8	8-8 (8)	6 (8)	75 (8)	180 (8)
	Fence between chambers	no adjustment	0.5	n/a-n/a (8)	6 (8)	75 (8)	180 (8)
7	Warehouse fumigation at a brewery facility	Study rate-not known					
	Applicators (structural PCOs)	no adjustment	1.1(study)	n/a-n/a (8)	2 (8)	n/a (8)	n/a (8)
	Aerators (structural PCOs)	no adjustment	0.6 (study)	n/a-n/a (8)	2 (8)	n/a (8)	n/a (8)
	Work areas (workers in fumigated building)	no adjustment	8 (6)	8-n/a (8)	3 (8)	n/a (8)	n/a (8)
Appen. C	2. Exposure of residents to MB from living near commodity fumigation facility						
	Low range of exposure days	no adjustment	24	24-n/a (8)	3 (6)	30 (6)	150 (6)
	High range of exposure days	no adjustment	24	24-n/a (8)	6 (6)	75 (6)	185 (6)

nonacute exposures include subacute, subchronic and chronic exposures.

section corresponds to that in Appendices B and C.

PCO = Pest control operator; BH = high barrier; VHB = very high barrier; PE = polyethylene.

an application rate that was used to adjust MB concentrations obtained from a study using a different application rate.

exposure times as indicated were used for the calculation of daily acute, subchronic (subchr.) and chronic (chr.) exposures (Tables B.1-B.18, C.1). n/a = not applicable.

References for those indicated under "Hours/workday" and "Workdays" in this table.

- 1. Methyl bromide proposed or suggested soil injection fumigation permit conditions (issued between 6/94 to 7/97).
- 2. Suggested permit conditions for methyl bromide soil fumigation within a greenhouse (issued between 9/94 to 9/96).
- 3. Suggested permit conditions for methyl bromide fumigation of tarped potting soil (issued between 12/95 to 9/96).
- 4. Based on MB product labels.
- 5. Based on Gibbons, 1994.
- 6. Based on Haskell, 1998a.
- 7. Based on Haskell, 1998b.
- 8. Assumed exposure times were based on Haskell (1998a, 1998b) or Gibbons (1994) for similarity in work practices. Only acute and subacute exposures were assumed for exposure in nonwork areas, such as fence line, lamp post, alleyway.
- 9. Sansone, 1998. (study) = from the study conducted by Gibbons, 1994.

# Appendix B Worker Exposure Studies

## Methyl bromide studies conducted in and after 1992

Daily acute, subchronic and chronic exposures for each of the following studies were calculated based upon appropriate MB air concentrations and daily duration of exposure for acute, subchronic and chronic exposures as shown in Appendix A. These exposure estimates and frequency of exposure (Appendix A) were used to calculate subacute, subchronic, and chronic exposures, which are shown in Table 11.

In the course of reviewing submitted exposure monitoring studies, numerous meteorological conditions (factors) in respect to air and soil temperatures, relative humidity, and wind conditions are available in several studies. However, it is rather impossible to determine the relationship or the effect of these conditions to MB concentrations that were used to estimate the exposure of workers. This is because collections of air samples were not sequentially made and the sample collection times were generally too short. Consequently, the analysis on the influence of meteorological conditions to MB concentrations was not conducted.

Also, some exposure monitoring studies were conducted before DPR issued suggested MB permit conditions. Some conditions used in these studies were not in compliance with current suggested permit conditions/regulations, such as an application of MB was done inside a greenhouse, an aeration period was shorter than that recommended in permit conditions, chambers were not pressure tested, or chambers did not have standard stacks. Data from these studies are not included in this exposure document. Detailed explanations are shown in the text of this document.

Methyl bromide studies conducted in and after 1992 are shown as follows:

## 1. Preplant soil injection fumigation (including aeration, tarp removal)

Worker exposure studies during preplant soil injection fumigation with MB were conducted in treated fields, nurseries or greenhouses. The soil was typically prepared and was ready for planting crops. The tarpaulin was either used or not used depending on methods of fumigation. Information regarding fumigation methods are provided below.

<u>a) Shallow-shank tarp method for MB fumigation: Worker exposure</u> (Siemer & Associates, 1992a)

Report No. SM924096A-D (Final report).

Study director: S.R. Siemer, Ph.D. (Siemer & Associates, Inc.).

Compliance with GLP standards (40 CFR Part 160): This study was not conducted in compliance with GLP.

### Application information

Formulation: MB 99.5%, Tricon 67-33, Tricon 57-43, Tricon 80-20.

Application rate: 214-398 Lbs a.i./A.

Date of application: July 14, 1992 to August 6, 1992.

Location (area treated, acres): Hayward (12), Wasco (78, 78, 18.76), Salinas (20, 20), Union City (10-13, 10-13), Wasco (78, 78), Watsonville (17-20, 17-20, 17-20, 9-10).

Crops to be planted: Strawberries, roses, gladiolus.

Use of tarpaulin: Dow or Cadillac high barrier tarpaulin.

Application method: MB was injected into the soil using one type of application equipment. A tractor was equipped with a pair of Noble Plow shanks (horizontal V-shaped blades), which were used to inject MB at a depth of 10-12". The Noble Plows were mounted to the tool bar. The injection spacing was 12" between injection outlets, which were evenly spaced across the trailing edge of each Noble Plow blade. The effective swath width was 7 feet. Each end of the tool bar had a conventional vertical shank that was injecting MB into the soil. This tractor was also equipped with an overhead fan above the head of the applicator. The fan chamber was 17" in diameter by 21" in height and was attached to the canopy of the tractor directly over the seat of the applicator. The fan was approximately 11 feet above the ground. There was a pair of plastic air supply pipe ducts for co-pilot positioned to either side of applicator. In addition, there was an opening and closing shovel on the field side of the tool bar to open and close the soil over the leading edge of the plastic tarp.

The thickness of the plastic tarpaulin used to seal the MB in the soil was 1.0 mil (Dow HB, Cadillac HB or Armin). The end of the tarp was buried with soil at the beginning and ending of swath. The lapping edge of the tarp was continuously glued to the previously laid adjacent strip. The other side was covered with a continuous band of soil.

# MB air monitoring study

Work activities (monitoring time, replicates):

- 1. Applicator (tractor driver of application rig) (5.08-7.38 hrs, n=8)
- 2. Co-pilot (applicator assistant) (5.35-7.37 hrs, n=7)
- 3. Shovelman (assist in turning rig around at the end of row and sealing of row end and start of next) (4.1-7.08 hrs, n=9)
- 4. Tarp removers (5-6 days post-fumigation; tarp was cut using an ATV equipped with a cutting wheel; exposure was monitored for supervisor, tarp cutter, roper, truck loader) (1.83-1.93 hrs, n=3)

## Exposure monitoring equipment:

- 1. Sample collection tubes-400/200 mg petroleum charcoal (A and B tubes, SKC #226-38-02).
- 2. Personal air sampling pumps-SKC model #222-3 or 224-PCXR7. The flow rate was set at approximately 20 mL/min.
- 3. Air inlet of tube A was set at about 8 inches from the worker's mouth.
- 4. Sampling tubes were kept on dry ice during storage and transportation.

Recovery study: An average recovery was 69%.

### Exposure assessment

Air concentrations of MB in submitted reports were pre-adjusted using an average recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were adjusted for an application rate of 400 Lbs a.i./acre. One-half (10 ppb) of the MDL was used for any values reported as none detected. Results are shown in Tables B.1 to B.5. Acute and nonacute exposure estimates are shown in Table 11.

Table B.1. Exposure of applicators to methyl bromide (MB) during shallow shank-tarped soil injection fumigation.

				Adjusted	2	24-hour TWA (pp	b)
Test	Lbs MB	Hours	MB conc.	MB conc.	N	oble Plow shanks	**
No.	/A	monitored	ppm, v/v	ppm, v/v*	Acute	Subchr.***	Chr.***
924096A-1	398	5.32	0.903	1.25	303	303	n/a
924096A-3	398	5.4	ND	0.01	3	3	n/a
924096A-4	398	6.5	0.423	0.59	142	142	n/a
924096A-5	235	5.08	0.052	0.12	30	30	n/a
924096A-7	398	5.8	0.251	0.35	84	84	n/a
924096A-9	398	5.43	0.245	0.34	82	82	n/a
924096A-11	214	7.38	0.087	0.22	54	54	n/a
924096A-13	280	5.92	0.397	0.78	189	189	n/a
				AVERAGE	111	111	n/a
				STDEV	98	98	n/a

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

<sup>\*</sup>adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999). One-half of the MDL (0.01 ppm) was used for non-detects.

<sup>\*\*</sup>with a fan operating over the applicator's head; a reduced number of conventional shanks; the system consisted of a pair of horizontal V-shaped blades (Noble Plow shanks); injection depth was 10-12"; had opening and closing shovels to open and close soil over the leading edge of the plastic tarpaulin.

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

Table B.2. Exposure of co-pilots to methyl bromide (MB) during shallow shank-tarped soil injection fumigation.

				Adjusted	24-hour TWA (ppb)			
Test	Lbs MB	Hours	MB conc.	MB conc.	N	loble Plow shanks	S**	
No.	/A	monitored	ppm, v/v	ppm, v/v*	Acute	Subchr.***	Chr.***	
924096A-1	398	5.35	1.546	2.14	518	518	n/a	
924096A-3	398	5.4	0.102	0.14	34	34	n/a	
924096A-4	398	6.5	0.792	1.10	265	265	n/a	
924096A-5	235	6.05	0.220	0.52	125	125	n/a	
924096A-7	398	5.77	0.772	1.07	259	259	n/a	
924096A-9	398	5.43	0.559	0.78	187	187	n/a	
924096A-11	214	7.37	0.285	0.74	178	178	n/a	
		_		AVERAGE	224	224	n/a	
				STDEV	152	152	n/a	

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

Table B.3. Exposure of shovelmen to methyl bromide (MB) during shallow shank-tarped soil fumigation.

				Adjusted	2	4-hour TWA (pp	b)
Test	Lbs MB	Hours	MB conc.	MB conc.	1	Noble Plow shanl	CS
No.	/A	monitored	ppm, v/v	ppm, v/v*	Acute	Subchr.**	Chr.**
924096A-1	398	5.47	0.459	0.64	154	n/a	n/a
924096A-1	398	5.3	0.490	0.68	164	n/a	n/a
924096A-4	398	5.77	0.337	0.47	113	n/a	n/a
924096A-4	398	5.83	0.201	0.28	67	n/a	n/a
924096A-5	235	5.6	0.184	0.43	104	n/a	n/a
924096A-7	398	4.1	0.366	0.51	123	n/a	n/a
924096A-9	398	5.02	1.536	2.13	515	n/a	n/a
924096A-11	373	7.08	0.146	0.22	52	n/a	n/a
924096A-13	280	4.53	0.252	0.50	120	n/a	n/a
924096A-13	280	4.47	0.122	0.24	58	n/a	n/a
				AVERAGE	147	n/a	n/a
				STDEV	135	n/a	n/a

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

<sup>\*</sup>adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*</sup>with a fan operating over the co-pilot's head.

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

<sup>\*</sup>adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*</sup>subchr. (subchronic) and chr. (chronic) are used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

Table B.4. Exposure of tarpaulin removers employed by pest control operators to methyl bromide (MB) during collection of tarp from shallow shank-tarped soil injection fumigation.

				Adjusted	24-hour TWA (ppb)		
Test	Lbs MB	Hours	MB conc.	MB conc.	Conventional shanks		
No.	/A	monitored	ppm, v/v	ppm, v/v*	Acute	Subchr.**	Chr.**
924096A-1	398	1.93	2.006	2.78	696	696	n/a
924096A-1	398	1.87	2.921	4.05	1013	1013	n/a
924096A-1	398	1.83	ND	0.01	3	3	n/a
924096A-1	398	1.8	2.321	3.22	805	805	n/a
924096A-1	398	0.63	4.785	6.64	1659	1659	n/a
				AVERAGE	835	835	n/a
				STDEV	596	596	n/a

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

Table B.5. Exposure of tarpaulin removers employed by growers to methyl bromide (MB) during collection of tarp from shallow shank-tarped soil injection fumigation.

				Adjusted	24-hour TWA (ppb)			
Test	Lbs a.i.	Hours	MB conc.	MB conc.	Conventional shanks			
No.	/A	monitored	ppm, v/v	ppm, v/v*	Acute	Subchr.**	Chr.**	
924096A-1	398	1.93	2.006	2.78	232	n/a	n/a	
924096A-1	398	1.87	2.921	4.05	338	n/a	n/a	
924096A-1	398	1.83	ND	0.01	1	n/a	n/a	
924096A-1	398	1.8	2.321	3.22	268	n/a	n/a	
924096A-1	398	0.63	4.785	6.64	553	n/a	n/a	
				AVERAGE	278	n/a	n/a	
				STDEV	199	n/a	n/a	

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

# b) Nontarp deep injection for measurement of MB exposure to the applicator, applicator assistant and cultipacker tractor driver (Siemer & Associates, 1992b).

Report No. SM924096B (interim report).

Study Director: S. R. Siemer (Siemer & Associates, Inc.).

Compliance with GLP standards: There was no GLP compliance statement in the report.

# Application information

Formulation: MB 99.5%.

Application rate: 398 Lbs a.i./A.

Date of application: (1992): July 15 (Chowchilla), July 28 (Shafter), October 21 (Shafter).

<sup>\*</sup>adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

One-half of the MDL (0.01 ppm) was used for non-detects.

\*\*subchr. (subchronic) and chr. (chronic) are used for the calculation of subchronic and chronic

exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

<sup>\*</sup>adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

One-half of the MDL (0.01 ppm) was used for non-detects.

<sup>\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

Location (area treated, acres): Chowchilla (25), Shafter (15), Shafter (15.2).

Use of tarpaulin: No.

Crop to be planted: Almond.

Application method: An application tractor was equipped with mounted tool bar. Shank injectors were set 20-24" deep, spaced up to 66" apart with a wing welded to the shank to break up the chisel chimney. The application tractor was followed by a disc-cultipacker to compact seal the soil surface. The tractor was equipped with a fan over an applicator's head.

## MB air monitoring study

Work tasks (monitoring time, replicates): Applicators (4.71-7.88 hrs, n=3), co-pilot (4.72, n=1), cultipacker tractor drivers (4.6-6.52, n=2).

Exposure monitoring equipment: Similar to those for shallow shank tarp fumigation.

Recovery study: An average recovery was 69%.

## Exposure/data assessment

Air concentrations of MB in submitted reports were pre-adjusted using an average recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were adjusted for an application rate of 400 Lbs a.i./acre. Results are shown in Table B.6. Acute and nonacute exposure estimates are shown in Table 11.

Table B.6. Exposure of applicators, applicator assistants and cultipacker tractor drivers to methyl bromide (MB) during deep shank injection.

	Lbs MB	Monitoring	MB conc.	Adjusted MB conc.		24-hr TWA (p	pb)			
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v**	Acute	Subchronic***	Chronic***			
Conventional deep shank injection (the tractor was equipped with a fan over an applicator's head)										
Applicator 1	398	4.72	0.377	0.52	126	126	n/a			
Applicator 2	398	7.88	0.539	0.75	181	181	n/a			
				Average	154	154	n/a			
Co-pilot	398	4.72	0.146	0.20	49	49	n/a			
Cultipacker 1	398	4.6	0.294	0.41	99	n/a	n/a			
Improved deep shank injection (the tractor was equipped with a fan over an applicator's head; used scrapers and press wheels on an application rig and the disc and drag bar on the second tractor pulling a cultipacker)										
Applicator 3	398	7.25	0.170	0.24	57	57	n/a			
Cultipacker 2	398	6.52	0.210	0.29	70	n/a	n/a			

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average.

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup> subchronic and chronic were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

c) Exposure of workers to MB during a deep shank, nontarp soil fumigation near Traver, Hanford, and Madera in California (Siemer & Associates, 1993a).

Report No.: SR934100.1A1 (April 16, 1993, interim report).

Study Director: S. R. Siemer (Siemer & Associates, Inc.).

Compliance with GLP standards: No detailed statement of GLP compliance.

## Application information

Formulation: 99% MB.

Application rate: 396 Lbs a.i./A.

Date of application: February 16, 1993.

Location (area treated): Traver, Hanford, and Madera in California.

Use of tarpaulin: No.

Crops to be planted: Not specified.

Application method (Basic equipment): An application tractor equipped with three forward curved shanks with 2x width of shank thickness chisel points (60" spacing) to inject MB to a depth of approximately 24 inches. The fumigation tractor was equipped with closing scrapers behind each of the three shanks, but not equipped with an overhead fan above the applicator.

The application tractor was equipped with a Type 2 air conditioned enclosed cab. Specific equipment used at each location is as follows:

- a) near Traver used basic equipment plus a second tractor with a disc that followed the application tractor.
- b) near Hanford used basic equipment plus a second tractor pulling a cultipacker that followed the application tractor.
- c) near Madera used basic equipment plus a second tractor pulling a cultipacker that followed the application tractor.

### MB air monitoring study

Work tasks (monitoring time, replicates): Applicator (2.72-6.53 hrs, n=3), disc driver (2.95 hrs, n=1), supervisor (3.28 hrs, n=1), cultipacker driver (2.95-6.2 hrs, n=2)

Exposure monitoring study: The exposure of workers to MB was measured by collecting air samples from the workers' breathing zone using charcoal sampling tubes during work activities.

Recovery: The average recovery was 69%.

### Exposure/data assessment

MB concentrations were adjusted for an application rate of 400 Lbs a.i./acre and a recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). Results are shown in Table B.7. Acute and nonacute exposure estimates are shown in Table 11.

Table B.7. Methyl bromide (MB) air concentrations near the workers' breathing zone and the estimation of worker exposure (non-tarp soil fumigation near Traver, Hanford and Madera in California.

	Lbs MB	Monitoring	MB conc.	Adjusted MB conc.	,	ıb)	
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v**	Acute	Subchr.***	Chr.***
Traver: Basic injection	n equipment plus a	second tractor with	a disc				
Applicator 1	396	2.72	0.26	0.36	88	88	n/a
Disc driver	396	2.95	1.52	2.12	512	512	n/a
Hanford and Madera:	Basic injection equ	nipment plus a secor	nd tractor pulling a	cultipacker			
Applicator 2	396	3.4	0.491	0.68	165	165	n/a
Applicator 3	396	6.53	0.066	0.09	22	22	n/a
				Average	94	94	n/a
Supervisor	396	3.28	0.198	0.28	67	67	n/a
Cultipacker 1	396	2.95	0.173	0.24	58	n/a	n/a
Cultipacker 2	396	6.2	0.03	0.04	10	n/a	n/a
				Average	34	n/a	n/a

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average.

# d) Deep shank, nontarp fumigation: Mitigation of MB worker exposure (near Helm, California) (Siemer and Associates, 1993b).

Report No.: SM934104.1-2, SM934104.2-1 (interim report) Study Director: S. R. Siemer (Siemer & Associates, Inc.)

Compliance with GLP standards: Not in compliance with GLP standards

#### Application information

Formulation: 97.6% MB/2.4% chloropicrin.

Application rate: 392 Lbs a.i./A. Date of application: March 8, 1993.

Location (area treated, acres): Near Helm, California (40).

Use of tarpaulin: No.

Crop to be planted: Grapes.

Application method: An application tractor was equipped with four forward curved shanks, each having a chisel point 2x wider than the width of the shank and an injector port forward of the leading edge of the shank body, behind the chisel point. The shanks were spaced 40 inches apart. The application tractor was equipped with a Type 2 air conditioned enclosed cab. Injection depth was approximately 27 inches. The shanks were each equipped with closing scrapers and followed by a gauge roller and a rolling cultipacker. During fumigation, shank slices were covered with soil from the use of closing scrapers. The soil was then compressed by the gauge roller. The soil in shank slices was further compressed by a cultipacker, which followed the application tractor within 5 minutes. In this improved deep soil injection fumigation method, a fan overhead of the applicator was not used.

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup> subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures shown in Table 11; hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

## MB air monitoring study

Work tasks (monitoring time, replicates): Applicator (9.18 hrs, n=1, cultipacker driver (8.38 hrs, n=1).

Exposure monitoring study: The exposure of workers to MB was measured by collecting air samples from the workers' breathing zone (approximately 8 inches from the mouth) using charcoal sampling tubes (400/200 mg charcoal) during work activities.

Recovery: The average recovery was 69%.

## Exposure/data assessment

Air concentrations of MB in submitted reports were pre-adjusted using a recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were adjusted for an application rate of 400 Lbs a.i./acre. Results are shown in Table B.8. Acute and nonacute exposure estimates are shown in Table 11.

Table B.8. Methyl bromide (MB) air concentrations near the workers' breathing zone and the estimation of worker exposure (deep shank non-tarp soil fumigation near Helm, California).

	Lbs MB	Monitoring	MB conc.	Adjusted MB conc.	24-hr TWA (ppb)			
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v**	Acute	Subchr.***	Chr.***	
Applicator	392	9.18	0.02	0.03	7	7	n/a	
Cultipacker	392	8.38	0.02	0.03	7	n/a	n/a	

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average.

### e) Shallow shank, tarped-bed soil fumigation: Worker exposure (Siemer & Associates, 1992c).

Report No. (status): SM924096 C, M (Interim report)

Study Director: S. R. Siemer & Associates, Inc.

Compliance with GLP standards: There was no information on GLP compliance.

# Application information

Formulation: 75% MB.

Application rate: 187.5 Lbs a.i./A.

Date of application: 10/92 and 11/17-18/92.

Location: Santa Maria. Use of tarpaulin: Yes.

Crop to be planted: Strawberries.

Application methods: An application rig was equipped with three 6- to 8-inch shanks, closing rollers, and tarp-laying equipment plus scrapers (closing shoes) mounted between the trailing edge of each shank and the closing roller. The scrapers were mounted to be rigid laterally and

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup> subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures shown in Table 11; hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

pivot vertically; their leading edge was forward of the trailing edge of each shank. The scrapers kept soil heaped on the base of each shank and traveled just under the soil surface so that soil and trash flowed over them. Soil injection was 6-8 inches below bed top.

# MB air monitoring study

Work tasks (monitoring time, replicates): Applicator (6.07-7.83 hrs, n=6), co-pilot (6.05-7.7 hrs, n=8), shovelman (7.1 hrs, n=2).

Exposure monitoring equipment: The exposure of workers to MB was measured by collecting air samples from the workers' breathing zone using charcoal sampling tubes (400/200 mg charcoal) during work activities.

Recovery study: An average recovery was 69%.

### Exposure assessment

Air concentrations of MB in submitted study reports were adjusted using a recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 250 Lbs a.i./acre. Results are shown in Table B.9. Acute and nonacute exposure estimates are shown in Table 11.

Table B.9. Exposure of workers to methyl bromide during (MB) fumigation using conventional and modified injection shanks.

	Lbs MB	Monitoring	MB conc.	Adjusted MB conc.	24-hr TWA (ppb)					
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v**	Acute	Subchr.***	Chr.***			
Conventional injection shanks plus the raised co-pilot platform and an injection depth of 8"										
Applicator	187.5	7.33	0.18	0.33	80	80	n/a			
Co-pilot	187.5	7.3	0.25	0.46	111	111	n/a			
Co-pilot	187.5	7.25	0.22	0.40	98	98	n/a			
				Average	104	104	n/a			
Conventional inj	ection shanks p	olus closing shoe	es							
Applicator	187.5	6.07	0.10	0.18	44	44	n/a			
Co-pilot	187.5	6.22	0.47	0.86	209	209	n/a			
Co-pilot	187.5	6.05	0.28	0.52	125	125	n/a			
				Average	167	167	n/a			

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average.

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for an application rate of 250 lbs MB/A (soil injection fumigation permit conditions, 12/95) and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

## f) Tarped-bed fumigation: Mitigation of MB worker exposure (Siemer & Associates, 1993c).

Report No. (status): SM934104.1M (interim report).

Study Director: S. R. Siemer (Siemer & Associates, Inc.)

Compliance with GLP standards: There was no information on GLP compliance.

## Application information

Formulation: 75% MB/25% chloropicrin (Tri-Con 75/25).

Application rate: 262.5 Lbs a.i./A. Date of application: February 15, 1993.

Location (area treated, acres): Arvin, Kern County, CA (≅ 20 acres).

Use of tarpaulin: 1.5 mil black mulch film.

Crop to be planted: Peppers.

Application method: MB was applied by a two-stage method. One tractor, Kennco Combi Superbedder, was equipped with swept back shanks spaced approximately 10" apart. This Supperbedder formed three beds (height-10," width-36") and injected MB to finished beds from outlets at the end of each shank at a depth of 10-14". The shanks were positioned so that they would extend between the bed puller blades, just ahead of the bed shaper, with soil covering them to a depth of 18 to 24" during bed formation. The finished bed injection depth was approximately 12-14". Drip tape was laid from the fumigation tractor. The 6 foot wide plastic tarp was carried on a bar on the second tractor. The plastic tarp was unrolled and covered the beds. Press wheels held the tarp in place on the sides of the beds while shovels threw soil over the edge of the plastic.

## MB air monitoring study

Work tasks (monitoring time, replicates): a) fumigation tractor-driver (7.77 hrs, n=1), applicator (7.72 hrs, n=1), tape layer (7.17 hrs, n=1); b) tarp laying tractor-driver (7.73 hrs, n=1), copilot (7.5 hrs, n=2).

Exposure monitoring equipment: The exposure of workers to MB was measured by collecting air samples from the workers' breathing zone using charcoal sampling tubes (400/200 mg charcoal) during work activities.

Recovery: A recovery of 88% was obtained by fortifying control samples with injecting standard.

## Exposure assessment

Air concentrations of MB in submitted study reports were adjusted using a recovery of 88%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 250 Lbs a.i./acre. Results are shown in Table B.10. Acute and nonacute exposure estimates are shown in Table 11.

Table B.10. Exposure of workers to methyl bromide (MB) during application using exposure mitigation method.

	Lbs MB	Monitoring	MB conc.*	Adjusted MB conc.**	24-hr TWA (ppb)				
Work task	/A	time (hrs)	ppm, v/v	ppm, v/v	Acute	Subchr.***	Chr.***		
The tractor was equipped for methyl bromide fumigation									
Driver	262.5	7.77	0.07	0.12	28	28	n/a		
Applicator	262.5	7.72	0.11	0.18	45	45	n/a		
Drip tape layer	262.5	7.17	0.16	0.27	65	65	n/a		
The tractor was e	quipped for l	aying tarp							
Driver	262.5	7.73	ND	0.02	4	4	n/a		
Co-pilot 1	262.5	7.5	0.16	0.27	65	65	n/a		
Co-pilot 2	262.5	7.5	ND	0.02	4	4	n/a		
				Average	34	34	n/a		

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average.

# g) Tarped-bed fumigation for measurement of MB exposure to the applicator, applicator assistant, and shovelman (Siemer & Associates, 1994)

Report No. (status): SM934110 (Interim report).

Study Director: S. R. Siemer (Siemer & Associates, Inc.).

Compliance with GLP standards: This study was conducted in compliance with GLP standards (40 CFR Part 160) with some exceptions. A signed copy of the compliance statement was attached to the submitted report.

# Application information

Formulation: 98% MB

Application rate: 287 Lbs a.i./treated acre

Date of application: July 13, 1993

Location (area treated, acres): Santa Maria, CA (9 acres)

Use of tarpaulin: 1.75 mil tarp Crops to be planted: Strawberries

Application method: The soil was fumigated by using a modified method of injection with swept-back shanks and a closing device for sealing off the shank slice. Three sweptback-style shanks were spaced approximately 10 inches apart. MB was injected through a series of hoses, valves and tubing to an outlet at the end of each shank. The shanks were positioned so that the injection port was extended backwards underneath the compaction roller. A closing device was situated to close the shank slice between the shank and the press roller. The injection depth was 6-8 inches. The closing device moved soil over the shank slice and the

<sup>\*</sup>adjusted by the study director for an a recovery of 88%. One-half of the MDL (10 ppb) was used for nondetects.

<sup>\*\*</sup> adjusted by DPR for an application rate of 250 lbs MB/A (soil injection fumigation permit conditions, 12/95) and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

compaction roller pressed the soil into the shank slice ahead of the plastic tarpaulin simultaneously laid over the top and side of the bed. The preformed beds measured 12-14 inches high and approximately 41 inches wide. The application tractor was not equipped with an overhead fan.

## MB air monitoring study

Work tasks (monitoring time, replicates): Applicator (10.33 hrs, n=1), applicator assistant (7.98 and 8 hrs, n=2), and shovelmen (9.32 and 7.83 hrs, n=2).

Exposure monitoring equipment: Air samples were collected by using a sampling train that consisted of two charcoal tubes containing 400 and 200 mg of charcoal and a personal sampling pump. Air intake ends of the sampling tube was positioned approximately 8 inches from the worker's mouth. The pump flow rate was approximately 20 mL/min.

Recovery study: An average recovery was 69%.

# Exposure/data assessment

Air concentrations of MB in submitted study reports were adjusted using a recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 250 Lbs a.i./acre. Results are shown in Table B.11. Acute and nonacute exposure estimates are shown in Table 11.

Table B.11. Exposure of handlers to methyl bromide (MB) during shallow shank, tarped-bed fumigation.

	Lbs MB	Monitoring	MB conc.	Adjusted MB conc.**	24-hr TWA (ppb)			
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v	Acute	Subchr.***	Chr.***	
Applicator	287	10.33	0.012	0.01	2	2	n/a	
Co-pilot A	287	7.98	0.108	0.13	31	31	n/a	
Co-pilot B	287	8.00	0.109	0.13	32	32	n/a	
				Average	32	32	n/a	
Shovelman A	287	9.32	0.002	0.002	0.6	n/a	n/a	
Shovelman B	287	7.83	0.002	0.002	0.6	n/a	n/a	

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

On July 7, 1998, DPR issued a memo to county agricultural commissioners informing them that the installation of sprinkler irrigation pipe during soil fumigation is not recognized in the current suggested soil permit conditions for MB (Sanders and Andrews, 1998). Some growers would like to continue the practice because the water from the sprinkler system may help keep the tarpaulin in place in windy conditions. However, the memo mentioned that preliminary data collected early in the permit condition development showed this procedure could result in serious overexposure to workers involved in pipe installation. Therefore, exposure data for irrigation pipe tractor drivers and pipelayers in the submitted report are not included in this exposure assessment document.

# h) MB exposure to the tarpaulin cutter and remover positions from tarped-shallow broadcast fumigation (TriCal, 1993a).

Report No. (status): TC211 (interim report).

Study Director: TriCal, Inc.

Compliance with GLP standards: This study was not conducted in compliance with GLP

standards (40 CFR Part 160).

## **Application information**

Formulation: MB 99.5% (Burrell and Corcoran), 80% (Watsonville).

Application rate (Lbs a.i./A): 298.5 (Burrell), 398 (Corcoran), and 280 (Watsonville).

Date of application: April 4, 12, and 28, 1993

Location (area treated, acres): Burrell (10.74 acres), Corcoran (10.48 acres), Watsonville (8.07

acres).

Use of tarpaulin: Dow HB or Cadillac HB.

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for an application rate of 250 lbs MB/A (soil injection fumigation permit conditions, 12/95) and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

Crops to be planted: Grapes, flowers, turf.

Application method: The broadcast fumigation of MB was made with Noble Plow shanks at the depth of 10-12". The tarpaulin was left in place for a minimum of five days after the completion of fumigation. After the five-day waiting period, each tarp panel was cut by a four wheeler using a cutting coulter. The aeration period for MB after the tarp cutting was completed in one day. At the end of the aeration period, tarp removal proceeded by windrowing the plastic panels and then pulling these panels into a truck for disposal.

## MB air monitoring study

Work tasks (monitoring time, replicates): Tarpaulin cutters (driver) (0.52-1.23 hrs, n=3), tarpaulin pullers or removers (e.g. tractor drivers, end rollers) (1.09-2.1 hrs, n=12).

Exposure monitoring equipment: Air samples were collected by using a sampling train consisting of two charcoal tubes containing 400 and 200 mg of charcoal and a personal sampling pump. Samples were taken from the breathing zones of the tarpaulin cutter and puller positions.

Recovery: The average recovery was 69%.

## Exposure/data assessment

Air concentrations of MB in submitted study reports were adjusted using the average recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 400 Lbs a.i./acre. Results are shown in Table B.12. Acute and nonacute exposure estimates are shown in Table 11.

Table B.12. Exposure of tarp cutters and removers to methyl bromide (MB).

				Adjusted			
	Lbs MB	Monitoring	MB conc.	MB conc.**		24-hr TWA (pr	
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v	Acute	Subchr.***	Chr.***
(By PCOs - work tin							
Cutter 2	298.5	0.52	ND	0.02	5	5	n/a
Cutter 1	398	1.1	ND	0.01	3	3	n/a
Cutter 1	280	1.23	0.48	0.95	237	237	n/a
				Average	82	82	n/a
				STDEV	134	134	n/a
(By growers - work t	time is 2 hours	/day)		Average	27	n/a	n/a
Cutters	inic is 2 nours	(day)		STDEV	45	n/a	n/a
Cutters				SIDEV	43	11/ a	11/α
(By PCOs - work tin	ne is 6 hours/d	ay)					
Puller 1(a)	298.5	2	ND	0.02	5	5	n/a
Puller 2(b)	298.5	2	ND	0.02	5	5	n/a
Puller 3(b)	298.5	2	0.7	1.29	324	324	n/a
Puller 1	398	2.1	0.04	0.06	14	14	n/a
Puller 2	398	2.08	ND	0.01	3	3	n/a
Puller 3	398	1.6	ND	0.01	3	3	n/a
Puller 1	280	1.17	ND	0.02	5	5	n/a
Puller 2	280	1.21	0.03	0.06	15	15	n/a
Puller 3	280	1.2	ND	0.02	5	5	n/a
Puller 4	280	1.12	ND	0.02	5	5	n/a
Puller 5	280	1.09	ND	0.02	5	5	n/a
Puller 6	280	1.1	ND	0.02	5	5	n/a
				Average	33	33	n/a
				STDEV	92	92	n/a
(By growers - work t	tima is 2 hours	/dow)		Average .	11	n/a	n/a
Pullers	inne is 2 nours	(uay)		STDEV	31	n/a	n/a n/a
Lis MD/A is the estimate	1: t / A . TXX /	. : . 4:: -1.4. 4	CTDEV		31	II/a	II/a

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

## i) Worker exposure to MB during tarp cutting and removal (TriCal, 1993b).

Report No. (status): TC233.3 (interim report). Study Director: Kirk Fowler (TriCal, Inc.).

Compliance with GLP standards: This study was not conducted in compliance with GLP standards (40 CFR Part 160).

# Application information

Formulation: 99.5% MB.

Application rate: 390.2 Lbs a.i./A. Date of application: October 19, 1993.

Location (area treated, acres): Gonzales, California (7.09 acres).

<sup>(</sup>a) end roller (b) tractor driver

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for an application rate of 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999). One half of the MDL (0.01 ppm) was used for nondetects.

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

Use of tarpaulin: 1.0 mil high barrier test film.

Crops to be planted: Head lettuce.

Application method: MB was injected into the soil at a depth of 10 inches using Noble Plow shanks. The fumigated area was thereafter covered with high barrier test film. The tarpaulin was left in place for at least five days after the complete of the application. After the five-day waiting period, each panel of the tarp was cut along the tape by an ATV equipped with a cutting wheel. After cutting and a 24-hour waiting period had elapsed, the tarpaulin was removed by workers.

# MB air monitoring study

Work tasks (monitoring time, replicates): Tarp cutter (0.36 hrs, n=1), Tarp remover (Tractor driver, basketman, end puller) (1.20-1.23 hrs, n=3).

Exposure monitoring equipment: MB levels were measured by collecting air samples from the workers' breathing zone using charcoal tubes (400/200 mg charcoal) for the duration of the work period.

Recovery: The average recovery was 69%.

## Exposure/data assessment

Air concentrations of MB in submitted study reports were adjusted using the average recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 400 Lbs a.i./acre. Results are shown in Table B.13. Acute and nonacute exposure estimates are shown in Table 11.

Table B.13. Exposure of tarp cutters and removers to methyl bromide (MB) following the use of high barrier tarpaulin.

				Adjusted					
	Lbs MB	Monitoring	MB conc.	MB conc.**	2	4-hr TWA (p	pb)		
Work task	/A	time (hrs)	ppm, v/v*	ppm, v/v	Acute	Subchr.***	Chr.***		
(By PCOs - work time is 6 hours/	day)								
Tarp cutter	390.2	0.36	0.22	0.31	78	78	n/a		
(By PCOs - work time is 6 hours/	day)								
Tarp remover 1 (Tractor driver)	390.2	1.2	0.97	1.37	343	343	n/a		
Tarp remover 2 (Basketman)	390.2	1.21	0.92	1.30	325	325	n/a		
Tarp remover 3 (End puller)	390.2	1.23	0.02	0.03	7	7	n/a		
(By growers - work time is 2 hour	rs/day)								
Tarp cutter					26	n/a	n/a		
(By growers - work time is 2 hours/day)									
Tarp remover 1 (Tractor driver) 114 n/a n									
Tarp remover 2 (Basketman) 108 n/a n/a									
Tarp remover 3 (End puller)					2	n/a	n/a		

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average.

# 2. Soil fumigation in nurseries and greenhouses

a) Worker exposure assessment during potting soil fumigation (Siemer & Associates, 1992d)

### Exposure study assessment

Exposure data from this study are not included in this exposure assessment document because the application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) The soil pile size was 6,000 yd<sup>3</sup> (permit conditions allow 400 yd<sup>3</sup>).
- b) The soil pile was tarped for 2 days (permit conditions require 3 days).

# b) Exposure of workers to MB during soil fumigation in greenhouses (Siemer & Associates, 1992e)

#### Exposure study assessment

Exposure data from this study, except exposure of tarp venters and tarp removers, are not included in this exposure assessment document because the application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) MB was introduced from inside the greenhouse (permit conditions require introduction of MB from outside the greenhouse).
- b) No information on leak checking of all fittings, connections, and valves of the introduction plumbing.

<sup>\*</sup> adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> adjusted by DPR for an application rate of 400 lbs MB/A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup>subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures (Table 11); hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

Details of the study are as follows:

Report No. (status): SM924099A1 (interim report).

Study Director (company): S. R. Siemer (Siemer and Associates, Inc.).

Compliance with GLP standards: There was no information to determine whether the study was conducted in compliance with GLP standards.

# Application information

Formulation: 99.5% MB.

Application rate: 447.75 Lbs a.i./A.

Date of application: August and September, 1992.

Location (area treated, acres): Oxnard, Ventura County (approximately 3/4 acres).

Use of tarpaulin: One mil high density tarpaulin.

Application method: Each plot of soil in a greenhouse to be treated with MB measured 20 feet wide by 150 feet in length. The applicator brought the fumigation trailer, which was used for heating the gas, to the east opening in the building. After all workers had cleared the area, the gas tank was connected to the heater coils that were heated by a propane burner. From the heater coils another hose was connected to the main PVC plastic pipe feeder. Hot MB was released through the plastic pipe manifold to which were attached a series of perforated plastic hoses. These hoses ran along the surface of the soil under preplaced tarpaulin.

Three days after the completion of fumigation, the tarp was cut open by hand using knives with elongated handles. The strips of the tarp were pulled apart and the greenhouse was allowed to vent for 48 hours. At the end of the venting period, the tarp was pulled and disposed.

#### Air monitoring study

Work tasks (monitoring time, replicates): Applicator (1.17-1.73 hrs, n=2), tarpaulin venter (0.35-0.65 hrs, n=4), tarp remover (1.03-1.37 hrs, n=4).

Exposure monitoring equipment: The exposure was measured by collecting air samples from the workers' breathing zone using charcoal sampling tubes (400/200 mg charcoal) connected to a personal air sampling pump. The flow rate was approximately 20 mL/min.

Recovery: The average recovery was 69%.

Exposures of tarp venters (must wear a SCBA) and tarp removers are included in this exposure assessment document because the aeration method was done in compliance with the permit conditions. Air concentrations of MB were adjusted using the average recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 6 Lbs MB/1,000 ft<sup>3</sup>. Results are shown in Tables B.14. Acute and nonacute exposure estimates are shown in Table 11.

Table B.14. Exposure of tarp venters and removers to methyl bromide (MB) during soil fumigations in greenhouses

	Lbs MB	Monitoring	MB conc.	MB conc.**		24-hr TWA (1	
Work task	/A	time (hrs)	ppm, v/v*	ppb, v/v	Acute	Subchr.***	Chr.***
Tarp venter 1	447.75	0.4	5.766	0.800	0.03332	n/a	n/a
Tarp venter 2	447.75	0.35	0.229	0.032	0.00132	n/a	n/a
Tarp venter 3	447.75	0.6	0.01	0.001	0.00006	n/a	n/a
Tarp venter 4	447.75	0.65	0.461	0.064	0.00266	n/a	n/a
				Average	0.00934	n/a	n/a
				STDEV	0.01602	n/a	n/a
Tarp remover 1	447.75	1.03	0.038	52.704	2.20	n/a	n/a
Tarp remover 2	447.75	1.03	0.017	23.578	0.98	n/a	n/a
Tarp remover 3	447.75	1.37	0.004	5.548	0.23	n/a	n/a
Tarp remover 4	447.75	1.32	0.007	9.709	0.40	n/a	n/a
				Average	0.95	n/a	n/a
				STDEV	0.89	n/a	n/a

Lbs MB/A is Lbs active ingredient/A; TWA is time-weighted average; STDEV is standard deviation.

# 3. MB monitoring: The Grain Product Group (Hosoda, 1992)

# Exposure study assessment

Exposure data from this study, except exposure of aerators and forklift drivers, are not included in this exposure assessment document because the application of MB was not conducted according to current permit conditions/regulations. An example:

a) No information on leak checking of all fittings, connections, and valves of the introduction plumbing.

Details of the study are as follows:

Report No. (status): Not assigned (Final report).

Study Director (company): Ed Hosoda (Cal Ag-Industrial Supply, Inc.).

Compliance with GLP standards: There was no information to determine whether the study was conducted in compliance with GLP standards.

#### Application information

Formulation: Methyl Bromide 100.

Application rate: 1.5-2 Lbs a.i./1,000 ft<sup>3</sup>. Date of application: May to August, 1992.

Locations: West Sacramento, Modesto, and Maxwell. Use of tarpaulin: 6 mil polyethylene tarpaulin, if used.

Application method:

<sup>\*</sup> Adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> Adjusted by DPR to reflect an application rate of 450 lbs MB/A, 50% recovery (Biermann and Barry, 1999; Helliker, 1999), and a protection factor of 10,000 for SCBA (NIOSH, 1987) worn by tarp venter.

<sup>\*\*\*</sup> subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures shown in Table 11; hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

- a) Fumigation applicators: MB was introduced from a cylinder into sea containers through <sup>1</sup>/<sub>4</sub>" polyethylene tubing. The application rate was 2 Lbs MB/1,000 ft<sup>3</sup>.
- b) Worker at initiation of aeration of sea containers/truck trailers: The workers opened both doors of the container and placed an insect screen to exclude reentry of flying insects. Eighteen-inch, 10,000 cfm "Patton" fans were left running for the entire aeration period of 24 hours.
- c) Forklift drivers emptying sea containers/truck trailers: Each container had been previously aerated for approximately 24 hours, and had no detectable amount of MB when using a Draeger MB 5/b tube. A forklift operator took about 15 minutes to unload each container contents and place produce inside the warehouse.
- d) Workers at initiation of aeration of tarpaulin fumigation: A tarp-covered stack of 1,000 ft<sup>3</sup> of blackeye beans was fumigated with 1.5 Lbs MB. The worker removed bags of beans from the outside edge of the tarps, then lifted the edges of the tarps and removed them from the entire stack.
- e) Forklift drivers emptying noncertified fumigation chambers: Two noncertified chambers with 2,500 ft<sup>3</sup> capacities were used in this study. Each chamber held a variety of rice products, with varying types of packaging. These chambers were aerated until air concentration of MB was below 5 ppm as measured with Draeger MB 5/b tube. Then the forklift operators were allowed to enter the chamber.

# Air monitoring study

Work tasks (monitoring time, replicates): Applicators (19.5-34 min, n=3), workers at initiation of aeration of sea containers/truck trailers (3.5-8.5 min, n=3), workers at initiation of aeration of tarpaulin fumigation (4-7 min, n=3), forklift drivers emptying sea containers/truck trailers (22-41 min, n=3), forklift drivers emptying noncertified fumigation chambers (17-32.5 min, n=3).

Exposure monitoring equipment: The exposure was measured by collecting air samples from the workers' breathing zone using charcoal sampling tubes (400/200 mg charcoal) connected to a personal air sampling pump. The monitoring method followed was that recommended in "Cal/EPA, DPR Methodology for Measuring MB Exposure to Workers" (Ross and Gibbons, 1992). The two charcoal tubes can handle the maximum air volume of 11 liters.

Recovery: The average recovery was 69%.

Exposures of aerators (must wear a SCBA) and forklift drivers are included in this exposure assessment document because the aeration method was done in compliance with the permit conditions. Air concentrations of MB were adjusted using the average recovery of 69%. However, the air concentrations were readjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999). MB concentrations were further adjusted by DPR for an application rate of 6 Lbs MB/1,000 ft<sup>3</sup>. Results are shown in Tables B.15. Acute and nonacute exposure estimates are shown in Table 11.

Table B.15. Exposure of workers to methyl bromide (MB) during and after fumigation of grain products.

	Lbs MB/	Monitoring	MB conc.*	MB conc.**		24-hr TWA (p	
Work task	1,000 ft3	time (min)	ppm, v/v	ppm, v/v	Acute	Subchr.***	Chr.***
Workers at initia	ation of aeration	of sea containers	s/truck trailers				
Aerator 1	2	6	1.303	0.0005	0.13	0.15	0.11
Aerator 2	2	3.5	8.028	0.0033	0.83	0.90	0.69
Aerator 3	2	8.5	8.172	0.0034	0.85	0.92	0.70
				Average	0.60	0.65	0.50
				STDEV	0.41	0.44	0.34
Workers at initia	ation of aeration	of tarpaulin fun	igation				
Aerator 1	1.5	4	ND	0.00001	0.001	0.001	0.001
Aerator 2	1.5	7	0.526	0.00029	0.073	0.079	0.060
Aerator 3	1.5	7	ND	0.00001	0.001	0.001	0.001
				Average	0.025	0.027	0.021
				STDEV	0.041	0.045	0.034
Forklift drivers	emptying sea co	ntainers/truck tra	ailers				
Driver 1	2	22	ND	0.04	2	1	1
Driver 2	2	41	0.25	1.04	43	22	22
Driver 3	2	25	0.01	0.04	2	1	1
				Average	16	8	8
				STDEV	24	12	12
Forklift drivers	emptying non-ce	rtifying fumigati	on chambers				
Driver 1	2	17	0.041	0.17	7	4	4
Driver 2	2	30	0.044	0.18	8	4	4
Driver 3	2	32.5	0.025	0.10	4	2	2
				Average	6	3	3
				STDEV	2	1	1

Lbs MB/1,000 ft3 is Lbs active ingredient/1,000 ft3; TWA is time-weighted average; STDEV is standard deviation.

# 4. Determination of MB exposure during dried fruit and tree nut fumigation practice (Radian Corporation, 1992)

#### Exposure study assessment

Exposure data from this study, except fumigation of chambers (raisins), are not included in this exposure assessment document, because of the following reasons:

<u>Sea van.</u> The application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) No information on leak checking of all fittings, connections, and valves of the introduction plumbing.
- b) Buffer zone was not in place.

<u>Chamber (dried prunes).</u> The application of MB was not conducted according to current permit conditions/regulations. Examples:

<sup>\*</sup> Adjusted by the study director for an average recovery of 69%.

<sup>\*\*</sup> Adjusted by DPR to reflect an application rate of 6 lbs MB/1,000 ft3, 50% recovery (Biermann and Barry, 1999; Helliker, 1999), and a protection factors of 10,000 for SCBA (NIOSH, 1987) worn by aerators. One-half of MDL (0.01 ppm) was used for nondetects.

<sup>\*\*\*</sup> subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures shown in Table 11; hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

- a) No information on leak checking of all fittings, connections, and valves of the introduction plumbing.
- b) Leakage of chamber.
- c) Buffer zone was not in place.

<u>Big chamber fumigation (raisins)</u>. The application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) No information on leak checking of all fittings, connections, and valves of the introduction plumbing.
- b) No stack for aeration.
- c) Buffer zone was not in place.

<u>Chamber (raisins)</u>: The exposure data are included in this exposure assessment document because of low leakage of the chamber. Data are shown in Table B.16.

<u>Fumigation of two noncertified chambers (walnut, shelled and in-shell)</u>. The application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) No criteria for integrity of chambers.
- b) No information on leak checking of all fittings, connections, and valves of the introduction plumbing.
- c) No minimum aeration time.
- d) Buffer zone was not in place at that time.
- e) No cap of total MB can be used.
- f) Fumigation where people were present.

<u>Sea van aeration (dried unpackaged prunes).</u> The reason for deletion is: Data represent area sampling only.

Details of the study for chamber (raisins) are as follows:

Report No. (status): RCN 256-254-04-01 (final report)

Study Director (company): Radian Corporation

Compliance with GLP standards: The study was not conducted in compliance with GLP standards.

# **Application information**

Formulation: Not reported.

Application rate: 0.8-3.0 Lbs a.i./1,000 ft<sup>3</sup>. Date of application: August to October, 1992. Area treated: Sea/land containers, chambers.

Use of tarpaulin: No. Application method:

Chamber (contained raisins): Volume of two chambers were 45,000 and 55,000 ft<sup>3</sup>. Application rate = 1 lb MB/1,000 ft<sup>3</sup>. Hot MB was injected into the chambers from an outside source. The fumigation time was 24 hours. The chambers were aerated for 24

hours after the completion of fumigation. The fumigated products were removed by forklift to the production line for processing.

# Air monitoring study

Chamber (raisins): Fumigators, aerators, chamber worker, stem pickers, forklift driver, hopper operator, and areas. Sampling times ranged from 5 to 536 minutes. During the fumigation period, area samples were located at both sides of the chamber and attached directly to the cage. Leak check samples were collected at locations approximately 1 foot from the edge of the door. There was no information with respect to the time of collection and the distance of samples from the MB source for aeration and clearing samples.

Exposure monitoring equipment: The exposure was measured by collecting air samples from the workers' breathing zone (20 cm radius circle from the worker's nose and mouth) and work areas using charcoal sampling tubes (400/200 mg charcoal) connected to a personal air sampling pump.

Analysis: The contents of the sampling tube was emptied into a glass headspace vial. Benzyl alcohol was added and the vial was thermostated at 110 °C. The headspace gas was sampled and analyzed by a gas chromatograph equipped with an electron capture detector. A recovery study was not conducted.

Table B.16. Exposure of workers to methyl bromide (MB) during and after fumigation of dried fruit and tree nut products.

	Lbs MB	Monitoring	MB conc.*	MB conc.**		24-hr TWA (	
Work task	/1,000 ft3	time (min)	ppm, v/v	ppm, v/v	Acute	Subchr.***	Chr.***
Chamber (raisins):							
Fumigator 1	1	41	0.57	1.71	107	107	71
Fumigator 2	1	40	0.1	0.30	19	19	13
				Average	63	63	42
		2	0.04	1.02	- 1		42
Aerator 1	1	3	0.34	1.02	64	64	43
Aerator 2	1	3	0.16	0.48	30	30 47	20 31
				Average _	47	47	31
Clear chamber 1	1	9	7.5	22.50	1,406	1,406	938
Clear chamber 2	1	10	7.8	23.40	1,463	1,463	975
				Average	1,434	1,434	956
Stem picker 1	1	488	0.026	0.08	26	26	26
Stem picker 2	1	486	0.03	0.09	30	30	30
Stem prener 2	-	.00	0.02	Average	28	28	28
				_			
Forklift driver	1	536	0.02	0.06	3	3	1.0
Hopper operator	1	490	0.019	0.06	19	19	19
Area sampling							
Fumigation chambers	1	33	0.47	1.41	88	88	59
Fumigation cage	1	35	0.29	0.87	54	54	36
Leak check-chamber 4	1	30	0.094	0.28	6	n/a	n/a
Leak check-chamber 5	1	29	0.024	0.07	2	n/a	n/a
Leak check-chamber 5	1	2)	0.024	Average	4	n/a	n/a
				_			
Aeration-chamber 4	1	8	0.99	2.97	186	186	124
Aeration-chamber 5	1	9	0.25	0.75	47	47	31
				Average _	116	116	78
Clearing-chamber 4	1	20	0.14	0.42	26	26	18
Clearing-chamber 5	1	19	0.35	1.05	66	66	44
-				Average	46	46	31
Hopper area	1	498	0.002	0.01	2	2	2
Hopper area, duplicate	1	498	0.002	0.04	13	13	13
	•	.,,	0.015	Average	8	8	8
Stom minlron	1	470	0.029	0.00	20	20	20
Stem picker Stem picker, duplicate	1 1	479 479		0.09	29 30	29 30	29 30
Stem picker, duplicate Stem picker	1	479 486	0.03 0.024	0.09 0.07	30 24	30 24	30 24
Stem picker	1	486 475	0.024	0.07	24 24	24 24	24
bem piekei	1	7/3	0.024	Average	27	27	27
				STDEV	3	3	3

Lbs MB/1,000 ft3 is Lbs active ingredient/1,000 ft3; TWA is time-weighted average; STDEV is standard deviation.

<sup>\*</sup>There was no indication in the report if air concentrations were adjusted for a recovery.

\*\*Adjusted by DPR based on rates shown in Appendix A and 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*</sup>Subchr. (subchronic) and chr. (chronic) were used for the calculation of subchronic and chronic exposures shown in Table 11; hours/workday and workdays for subchronic and chronic exposures are shown in Appendix A.

5. MB: Measurement of exposure to the fumigators, forklift drivers, cherry sorters, and other workers (Stegmiller and Lee, 1992)

### Exposure study assessment

Exposure data from this study are not included in this exposure assessment document because the application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) Did not purge lines between cylinders.
- b) Control room storage.
- c) Leakage of chamber.
- d) Vent to control room.
- e) Aeration time was about 3 hours (PCs require a minimum aeration time of 4 hours by active aeration).
- 6. Worker exposure and on-site air monitoring studies at a walnut processing facility (Air Toxics LTD, 1995).

# Exposure study assessment

Some MB air concentrations from this report are not included in this exposure assessment document because the application of MB was not conducted according to current permit conditions/regulations. Examples:

- a) Worker exposure studies. The 1993 studies were conducted before DPR issued permit conditions. The 1994 study is used, except data obtained from a study at Dock 5 (leakage of MB to occupied area. The chamber was inside another building, and there was no retention test).
- b) Area sampling. Not for worker exposure assessment. Retain only exposure of sorters.
- c) On-site ambient air monitoring. Not for worker exposure assessment.
- d) <u>Compliance monitoring</u>. This exposure assessment document includes exposure of workers in processing areas. The study was conducted after DPR issued the permit conditions.

Details of the study are as follows:

Report No. (status): Not assigned (Final report).

Study Directors (company): Eric D. Winegar, David B. Curtis, Marie J. Yates (Air Toxics Limited).

Compliance with GLP standards: The study was not conducted in compliance with GLP standards.

#### Application information

Formulation: Not mentioned. Application rate: Not mentioned.

Date of studies: 1993 (October 27 and 28; December 20 and 21), and 1994 (March 17 and 18;

October 11 and 12).

Location: A walnut processing facility in Stockton.

Application method: The report indicated that methyl bromide was injected into Butler- or Polygon-type chambers. At the end of the fumigation period, chambers were aerated. The Butler chambers had a stack of sorts where the emission point was actually below the apex of the chamber. The Butler chambers were vented by a large fan system at the base of the chambers. The Polygon had no stack, only the openings at the top of the conical rooftop. These chambers were vented by a portable fan system that was inserted into an opening at the base of the chamber.

# Air monitoring study

Worker exposure and area monitoring: Exposure of workers performing duties in different work areas and area air concentrations are shown in Table B.17.

Exposure monitoring equipment: For worker exposure monitoring studies - Two or three tubes of petroleum charcoal sorbent (2 of 200 mg, or 1 of 200 mg and 2 of 100 mg) and personal air sampling pumps were used. The flow rate was 30-40 mL/min. For area and on-site ambient air monitoring studies, identical sampling and analytical methods as that in the worker exposure monitoring studies were used. In addition, a few samples were collected into stainless steel canisters and analyzed using the U.S. EPA Compendium method TO-14 (cryofocus GC/MS), which afforded a lower detection limits for those samples. The distance for area and on-site monitoring studies with respect to the source of MB could not be determined from the maps, which were included in the submitted report. The fumigation of walnuts during the peak of the season was continuous. The source of MB could be from the fumigation during the study or off-gassing from previously fumigated walnuts.

Air concentrations of MB from worker exposure and area monitoring studies were calculated and reported as the 24-hour TWA; monitoring times for replicates were not mentioned in the report. On-site ambient air concentrations of MB were reported as ppb; collection times for day- and night-monitoring periods were generally long.

Recovery: Recoveries ranged from 74 to 125%. There was no information to indicate that the exposures were adjusted for the recovery. However, the air concentrations were adjusted by DPR to reflect a recovery of 50% (Biermann and Barry, 1999; Helliker, 1999).

# Compliance monitoring study conducted by WH&S

On October 19, 1995, staff of the Worker Health and Safety Branch, DPR, conducted a full-shift monitoring study to determine the air concentration of MB at the four selected work stations at the Diamond Walnut facilities in Stockton (Gibbons, 1995). At each work station, three locations were chosen for the monitoring equipment. All samples were obtained as area samples and no personal samples were obtained. At all but one work station, the samplers were placed to sample air believed to be representative MB concentrations to which workers were being exposed. A representative of Air Toxics Limited also collected air samples from the same work stations. Results of this study were included in Table B.17 for comparison with those obtained from a study previously performed by Air Toxics Limited.

Table B.17. Methyl bromide (MB) air concentrations obtained from worker exposure studies, and area and on-site air monitoring studies at a walnut processing plant in Stockton.

	Work		24-hour T	WA (ppb)	
	area	10/1994*	Acute**	Subchr.**	Chr.**
a) Worker exposure studies	Bulk packaging	22	44		
		12	24		
		Average	34	34	n/a
	Cleaning plant	57	114		
		175	350		
		0.5	1		
		167	334		
		202	404		
		17	34		
		158	316		
		85	170		
		31	62		
		174	348		
		10	20		
		170	340		
		Average	208	208	n/a
		STDEV	155	155	n/a
	Fumigatorium	53	106		
	Ü	52	104		
		25	50		
		Average	87	63	39
		STDEV	32	23	14
	Packaging	22	44		
	Vacuum chamber	46	92		
	v acuum chamber	233	466		
		79	158		
		Average	239	239	n/a
		STDEV	200	200	n/a
	Sorting	10	200	200	11/ U
	bording	27	54		
		23	46		
		7	14		
		12	24		
		16	32		
		Average	32	32	n/a
		STDEV	16	16	n/a
	Special cracking	17	34	10	11/ a
	Special cracking	16	32		
		17	32 34		
		8			
			16 29	29	a- /-
		Average ('93- Average			n/a
TXX/A	TENEVI' . 1 11 '.	STDEV ('93-STDEV	9	9	n/a

TWA is time-weighted average; STDEV is standard deviation.

Table B.17 (cont.). Methyl bromide (MB) air concentrations obtained from worker exposure studies, and area and on-site air monitoring studies at a walnut processing plant in Stockton.

	Work		24-hour T	WA (ppb)	
	area	10/1994*	Acute**	Subchr.**	Chr.**
b) Area monitoring study	Sorting line	40	80		
		43	86		
		Average	83	n/a	n/a
c) Compliance monitoring (Gibbo	ons, 1995) (10/19/95).				
Sorting line in cleaning plant (12-h	nr shift)				
Nut exit - sorting line #	<b>‡</b> 1	287	287		
Nut exit - sorting line #	‡2	324	324		
Nut entrance manifold,	line #2	343	343		
		Average	318	318	n/a
		STDEV	28	28	n/a
Cello packaging of in-shell walnuts	s in main building (9-hr shift)				
Packing machine #11 -	power box	485	364		
Packing machine #9 - p	power box	435	326		
Column by boxing pers	son near #9	500	375		
		Average	355	355	n/a
		STDEV	26	26	n/a
Bulk packaging of in-shell walnuts	in main building (11-hr shift)				
Column by stitching st	ation	264	242		
Control panel - bag fill	ing	267	245		
On stitching machine		void			
		Average	243	n/a	n/a

TWA is time-weighted average; STDEV is standard deviation.

Acute, subchronic and chronic exposures were adjusted for 50% recovery.

# 7. Space-type fumigation: Potential worker exposure to MB at a brewery facility (Gibbons, 1994).

# Exposure study assessment

DPR conducted the monitoring study designed to gather data on potential worker exposure associated with the space-type fumigation at a brewery facility and during the aeration on the following day. Results are shown in Table B.18. The air concentrations shown are potential exposure and not actual exposure. Acute and nonacute exposure estimates are shown in Table 11.

Details of the study are as follows:

<u>Application information</u>
Formulation: Not mentioned
Application rate: Not mentioned

Date of application: November 26, 1992

Location (area treated): Fairfield (area was not known)

Use of tarpaulin: No

<sup>\*</sup> as shown in the submitted report. It was assumed that air concentrations were adjusted using the mid-point recovery (99.5%) of a recovery range of 74-125%.

<sup>\*\*</sup> The calculation procedure for daily nonacute exposures are as follows:

Daily subchronic MB conc. = (Daily acute MB conc. x daily subchronic exposure time (hrs)/daily acute exposure time (hours). The same method was used for the calculation of daily chronic exposures.

Application method: During the application of fumigation, two applicators wearing Self-Contained Breathing Apparatus (SCBA) made repeated entries into the grain storage and processing areas to open pre-placed small MB canisters and large cylinders. The canisters were used to treated the inside of numerous enclosed pipes and other equipment, which were used for transferring the grain. The large cylinders were used to treat the enclosed air spaces surrounding the equipment. After the fumigation was done, the fumigated area was left undisturbed for 24 hours. During the aeration phase, two workers wearing SCBA made two entries into the space to initiate the aeration. Work tasks during application and aeration are listed in Table B.18.

# Air monitoring study

Work tasks (monitoring time, replicates): Applicators (5-36 min, n=4), aerators (6-24 min, n=4).

Exposure monitoring equipment: Not reported

Recovery: Not reported

Table B.18. Monitoring of methyl bromide during space fumigation and aeration at a brewery facility.\*

Activity	Monit. time (minutes)	MB conc. (ppm)	Protection factor-PF**	Estimated exposure (ppb)	Estimated exposure, ppb*** (24-hr TWA)
a) Applicator (one applicator, 4 samples	(s))				
Appl. 1, s 1- entry to open canisters	14	298	10,000	29.8	
Appl. 1, s 2 - reentry to open canisters	36	3624	10,000	362.4	28.9
Appl. 1, s 3 - reentry to open canisters	11	3871	10,000	387.1	
Appl. 1, s 4 - reentry to open large cylinders	5	6117	10,000	611.7	
Area sample (door to buffer zone)	1530	635	10,000	63.5	42
b) Aerator (two aerators, 4 samples)					
Aerator 1, s 1	24	7016	10,000	701.6	24
Aerator 1, s 2	20	169	10,000	16.9	
Aerator 2, s 1	19	9546	10,000	954.6	25
Aerator 2, s 2	6	11.4	10,000	1.14	
				Average	25
Area sample (left of entrance door)****	70	0.26	n/a	260	173
Area sample (on applicator's truck)****	55	0.15	n/a	150	100

TWA is time-weighted average; n/a is not applicable.

<sup>\*</sup> Workers wore a SCBA during the application and aeration processes.

<sup>\*\*</sup> A protection factor (PF) (NIOSH, 1987) was used to derive estimated exposure.

<sup>\*\*\*</sup> Calculated based on serial sampling for an applicator and two aerators. It was assumed that the indicated monitoring times were similar to actual exposure times. Exposures were adjusted by DPR for 50% recovery (Biermann and Barry, 1999; Helliker, 1999).

<sup>\*\*\*\*</sup> Assumed workers may work in areas where samples were collected. Typically, these workers do not use a SCBA.

# 8. Grouping of MB acute exposure estimates of handlers during soil fumigation.

There are several worker exposure studies during soil fumigation as shown in Tables B.1 to B.13. Some of these studies have a limited number of replicates that cannot be used to generalize the magnitude of worker exposure. Grouping of these air concentrations is an exercise to evaluate the distribution of these data if they are normally or lognormally distributed. Thereafter, the range, mean and 95<sup>th</sup> percentile are calculated for the grouped data. Mitigation measures may not be developed based on these data because the measures are based on specific fumigation methods.

Acute MB air concentrations calculated as the 24-hour TWA are grouped as follows:

- 8.a) Air concentrations obtained from nonbedded and bedded fumigation
- 8.b) Air concentrations obtained from nonbedded soil fumigation
- 8.c) Air concentrations obtained from bedded soil fumigation
- 8.d) Air concentrations obtained from commodity, greenhouse, and space–type fumigations

# a) Air concentrations obtained from nonbedded and bedded fumigation

The following air concentrations were used for this grouping:

- 1). Shallow shank-tarped soil injection fumigation (Table B.1). Applicators: Noble plow shanks
- 2). Shallow shank-tarped soil injection fumigation (Table B.2). Co-pilots: Noble plow shanks
- 3). Shallow shank-tarped soil injection fumigation (Table B.3). Shovelmen: Noble plow shanks (by growers).
- 4). Deep shank injection fumigation (Table B.6). Applicators, co-pilots, cultipackers.
- 5). Deep shank injection fumigation (improved) (Table B.6). Applicators, cultipackers.
- 6). Deep shank injection fumigation (Table B.7). Applicators, disc drivers, supervisor, cultipacker tractor drivers.
- 7). Deep shank injection fumigation (Table B.8). Applicator, cultipacker tractor driver.
- 8). Shallow shank-tarped bed fumigation (Table B.9). Applicators, co-pilots.
- 9). Shallow shank-tarped bed fumigation (Table B.10). Applicators, co-pilots, tractor drivers, tape layers.
- 10). Shallow shank, tarped-bed fumigation (Table B.11). Applicators, co-pilots, shovelmen.

#### Results

- a) The tests of normality and lognormality indicated that both normality and lognormality are rejected. That is neither one fits.
- b) The range of the MB concentrations (n = 57): 1-518 ppb
- c) The arithmetic mean  $\pm$  STDEV = 123  $\pm$  120 ppb
- d) 95<sup>th</sup> percentile = Arithmetic mean + 1.671 (STDEV) = 324 ppb

# b) Air concentrations obtained from nonbedded soil fumigation

- 1). Shallow shank-tarped soil injection fumigation (Table B.1). Applicators: Noble plow shanks
- 2). Shallow shank-tarped soil injection fumigation (Table B.2). Co-pilots: Noble plow shanks

- 3). Shallow shank-tarped soil injection fumigation (Table B.3). Shovelmen: Noble plow shanks (by growers).
- 4). Deep shank injection fumigation (Table B.6). Applicators, co-pilots, cultipackers.
- 5). Deep shank injection fumigation (improved) (Table B.6). Applicators, cultipackers.
- 6). Deep shank injection fumigation (Table B.7). Applicators, disc drivers, supervisor, cultipacker tractor drivers.
- 7). Deep shank injection fumigation (Table B.8). Applicator, cultipacker tractor driver.

#### Results:

- a) The tests of normality and lognormality indicated that both normality and lognormality are rejected. That is neither one fits.
- b) The range of the MB concentrations (n = 40): 3-518 ppb
- c) The arithmetic mean  $\pm$  STDEV = 136  $\pm$  131 ppb
- d) 95<sup>th</sup> percentile = Arithmetic mean + 1.684 (STDEV) = 356 ppb

# c) Air concentrations obtained from bedded soil fumigation

- 1). Shallow shank-tarped bed fumigation (Table B.9). Applicators, co-pilots.
- 2). Shallow shank-tarped bed fumigation (Table B.10). Applicators, co-pilots, tractor drivers, tape layers.
- 3). Shallow shank, tarped-bed fumigation (Table B.11). Applicators, co-pilots, shovelmen.

#### Results:

- a) The tests of normality and lognormality indicated that both normality and lognormality are rejected. That is neither one fits.
- b) The range of the MB concentrations (n = 57): 1-334 ppb
- c) The arithmetic mean  $\pm$  STDEV = 93  $\pm$  87 ppb
- d)  $95^{th}$  percentile = Arithmetic mean + 1.740 (STDEV) = 245 ppb

# d) Air concentrations obtained from commodity, greenhouse and space–type fumigations.

1) Commodity: handlers.

Exposure during dried fruit and tree nut fumigation practice (Table B.14). Fumigators, aerators.

Exposure during fumigation of grain products - sea container/truck trailer, noncertified chambers (Table B.15). Aerators.

Worker exposure and on-site air monitoring studies at a walnut processing facility (Table B.17). Fumigators.

#### Results

- a) The range of the MB concentrations (n = 15): 0.001-186 ppb.
- b) The arithmetic mean  $\pm$  STDEV = 47.7  $\pm$  56.2 ppb.
- c)  $95^{th}$  percentile = Mean + 1.761 (STDEV) = 146 ppb.
- 2) Commodity: other workers.

Exposure during dried fruit and tree nut fumigation practice (Table B.14). Stem pickers and other area workers.

Worker exposure and on-site air monitoring studies at a walnut processing facility (Table B.17). Sorters and other area workers.

Exposure during fumigation of grain products - sea container/truck trailer, noncertified chamber (Table B.15). Drivers.

#### Results:

- a) The range of the MB concentrations (n = 52): 1-466 ppb.
- b) The arithmetic mean  $\pm$  STDEV =  $83 \pm 119$  ppb.
- c)  $95^{th}$  percentile = Mean + 1.678 (STDEV) = 283 ppb.

#### 3) Greenhouse:

Exposure of workers to MB during soil fumigation in greenhouse (Table B.14). Tarp venters.

#### Results:

- a) The range of the MB concentrations (n = 4): 0.0001-0.03 ppb.
- b) The arithmetic mean  $\pm$  STDEV = 0.009  $\pm$  0.016 ppb.
- c)  $95^{th}$  percentile = Mean + 2.353 (STDEV) = 0.047 ppb.

# 4) Greenhouse:

Exposure of workers to MB during soil fumigation in greenhouse (Table B.14). Tarp removers.

#### Results:

- a) The range of the MB concentrations (n = 4): 0.4-2.2 ppb.
- b) The arithmetic mean  $\pm$  STDEV =  $1.0 \pm 0.9$  ppb.
- c)  $95^{th}$  percentile = Mean + 2.353 (STDEV) = 3.1 ppb.
- 5) Brewery facility: Handlers.

Exposure replicates are not sufficient for grouping purposes.

Table B.19. Grouping of acute methyl bromide (MB) exposure estimates for workers during fumigations of soil, commodity and brewery facility<sup>a</sup>.

		MB concer	ntration (ppb)					
Types of fumigation	Replicate	Mean ± STDEV	Range	95 <sup>th</sup>				
				percentile				
Soil: Nonbedded & Bedded <sup>b</sup>	57	$123 \pm 120$	1 - 518	324				
Soil: Nonbedded <sup>b</sup>	40	$136 \pm 131$	3 - 515	356				
Soil: Bedded <sup>b</sup>	17	$93 \pm 87$	1 - 334	245				
Commodity: Handlers	15	$48 \pm 56$	0.001 - 186	146				
Commodity: Other workers	52	$83 \pm 119$	1 - 404	283				
Greenhouse: Tarp venters	4	0.01 - 0.02	0.0001 - 0.03	0.05				
Greenhouse: Tarp removers	4	$1.0 \pm 0.9$	0.4 - 2.2	3.1				
Brewery facility <sup>c</sup>	Exposure replicates are not sufficient for grouping purposes							

STDEV is standard deviation.

<sup>&</sup>lt;sup>a</sup> exposure estimates were grouped according to types of fumigations.

b exposure of handlers.

was not grouped because there are only 1 to 2 replicates for each exposure scenario.

# Appendix C Residential Exposure Studies

DowElanco submitted a study conducted by the University of Florida in support of sulfuryl fluoride registration (Bloomcamp *et al.*, 1991). The same report also contained data on MB indoor air concentrations after subsequent aeration of 10 fumigated homes. These homes were fumigated with MB at a rate of  $16 \text{ g/m}^3$  and thereafter aerated to 5 ppm according to U. S. EPA-approved procedures. However, the air concentration substantially increased (19.2  $\pm$  10.9 ppm) after the doors and windows were closed for two hours. Homes were aerated and closed again. During the second 2-hour closure, MB concentration increased above 5 ppm in four homes (18.6  $\pm$  5.4 ppm). This study was conducted to better characterize the fate of indoor air concentrations of the fumigant following aeration.

A second submitted report related to indoor fumigation was conducted because of a request to modify a method to release MB into the fumigated structure (Soil Chemicals Corp., 1980). Results from three tests indicated that equilibrium of the fumigant can be best achieved by shooting gas into the attic. Data indicated that the gas initially tends to move in a downward direction. When the gas was shot into the living space, the attic was the last area to reach equilibrium. This report did not provide appropriate indoor air concentration to estimate exposure of residents.

- 1. Residential exposure studies.
- a) Residents/bystanders (outdoor and indoor air concentrations of MB near fumigated single-family houses (Gibbons *et al.*, 1996a).

# Exposure study assessment

Exposure data from this study are not included in this exposure assessment document because the application of MB was not conducted according to current regulations (CCR, 2000). Example:

- a) The distance of air sampling stations is no longer valid based on current regulations.
- b) Residents/bystanders (downwind outdoor and indoor air concentrations of MB during aeration of fumigated single-family houses (Gibbons *et al.*, 1996b).

#### Exposure study assessment

Exposure data from this study are not included in this exposure assessment document because the application of MB was not conducted according to current regulations (CCR, 2000). An example:

- a) The aeration method used in the study is no longer valid based upon the new regulations for MB structural fumigation.
- 2. Exposure of residents to methyl bromide during reentry into fumigated houses (Gibbons, 1992).

Residents can be exposed to airborne MB after reentry into their fumigated houses following aeration. MB product labels require a minimum active aeration period (e.g., using fans) of 72

hours and the level of MB must be less than 3 ppm measured in the ground receptacle of an interior electrical outlet or other enclosed space within the wall or an interior and a perimeter wall. The aeration period must last for a minimum of 7 days if nonmechanical or natural ventilation is used. This exposure monitoring study of fumigated houses used only 24-hour aeration period.

# Exposure study assessment

Exposure data from this study are not included in this exposure assessment document because the application of MB was not conducted according to current regulations (CCR, 2000) and product labels. An example:

- a) The active aeration time was only 24 hours. Current product labels require a 72-hour active aeration period.
- 3. Exposure of residents to methyl bromide from living near commodity fumigation facility.

During commodity fumigation and aeration periods, leaks and off gassing with subsequent dilution can aid in dispersion of MB vapor into the surrounding areas. Residents who live at or beyond an established buffer zone may be exposed to airborne MB. The following assumptions were used to estimate exposure of residents to airborne residues of MB from commodity fumigation.

- a) Residents live at an established buffer zone. We did not attempt to estimate exposure of residents beyond the buffer zone.
- b) The wind blows continually from the fumigation areas toward residential areas in the same direction. This represents an extreme exposure scenario.
- c) Residents are assumed to be exposed to MB at the target level of 210 ppb calculated as the 24-hour TWA (Nelson, 1992).
- d) The housing structure does not provide protection from inhalation exposure to MB.
- e) There are intermittent fumigations of chambers in those areas contributing to exposure days of more than approximately 33% of days in a 7-day, 90-day or 365-day period. These exposures constitute subacute, subchronic and chronic exposures, respectively (Sanders, 1998). Likewise, if exposure days are less than the specified exposure frequency, there will be no subacute, subchronic and chronic exposures. Also, more frequent MB fumigations in those areas will result in maintaining the target exposure level at or close to the target level of 210 ppb.

The low and high ranges of exposure days for workers during commodity fumigations were adopted from Haskell (1998a, 1998b) for use in the estimation of residential exposure. Subacute, subchronic and chronic exposures are shown in Table C.1.

Table C.1. Exposure of residents to airborne methyl bromide during commodity fumigation<sup>a</sup>.

Range of	Subacu	Subacute exposure		c exposure	Chronic exposure		
exposure	/7days	MB (ppb)	/90 days	MB (ppb)	/365 days	MB (ppb)	
Low <sup>b</sup>	3	90	30	70	150	86	
High <sup>b</sup>	6	180	75	175	185	106	

a assumed residents are exposed to the target level of 210 ppb (24-hour TWA).

# 4. Exposure of residents to MB from living at the buffer zone distance.

Methyl bromide air concentrations at the buffer zone distance are needed for the determination of exposure of residents and workers, who live or work at the buffer zone distance. The air concentrations must reflect different field sizes, recommended application methods, and the maximum allowed application rates because the emission rates are varied based on these conditions. Hence, MB air concentrations based upon these conditions are not the same. Currently, there is no exposure study to measure MB concentrations at the buffer zones to reflect these conditions. MB concentrations at the buffer zones were generated by simulation technique.

Johnson (2001) provided detailed explanation as to how MB air concentrations at the buffer zone distance were estimated. The simulation consisted of daily (24-hour) simulations using the Industrial Source Complex-Short Term model 3 (ISCST3) version 99155. The simulations were designed to cover the proposed buffer zones for 1 to 40-acre fields with emission rates ranging from 30 to 225 lbs/acre-day. For the actual simulation, the emission rate of 225 lbs/acre-day was used. To obtain simulation results at lower emission rates, a post-processing computer program scaled the concentrations down proportionally, assuming emission and concentrations are proportional. The post-processing program with the construction of transects enable the estimation of proposed (daily) buffer zones (Johnson, 2001). The maximum MB concentrations at the buffer zone distances were determined for different emission rates and field sizes. The maximum MB concentrations ( $\mu$ g/m³) determined from the program for key percentiles are shown in the nonshaded (nonboxed) areas of Table C.2. MB air concentrations in the shaded (boxed) areas were interpolated to reflect other emission rates (100, 150, 160, 200 and 320 lbs/acre-day).

The column headings indicate emission rates, ranging from 30 to 320 lbs/acre-day. Methyl bromide concentrations ( $\mu g/m^3$ ) are shown in columns under emission rates. These concentrations are grouped according to the field sizes (1, 10, 20, 30, and 40 acres) and reflect different cumulative probability (0.1 to 0.999). The regulatory MB concentration level for acute exposure is 210 ppb, which is equivalent to 815  $\mu g/m^3$ . The highest air concentrations at the 95<sup>th</sup> percentile, which represent a range of emission rates in Table C.2 for 1, 10, 20, 30, and 40 acres were used to estimate the exposures. The method used to determine the highest MB concentration is given in the subsequent sections.

exposure days were based on Haskell, 1998a and 1998b. The low and high exposures represent the low and high exposure days for subacute, subchronic and chronic exposures.

Table C.2. Interpolated methyl bromide air concentrations (ug/m3, shaded or boxed areas) based on different emission rates and field sizes.\*

	Emission **	30	80	100	130	150	160	180	200	225	
	Cum. Prob.***				Methyl bror	mide concer	ntration (ug/	m3)			
1 acre	0.1	95	240	238	234	229	227	222	220	217	206
	0.2	109	278	277	275	270	267	262	260	257	246
	0.3	122	310	309	308	302	300	294	292	290	282
	0.4	133	339	339	340	334	332	326	323	320	307
	0.5	144	369	371	373	367	365	359	357	354	343
	0.6	157	401	404	408	404	402	398	394	390	373
	0.7	172	439	445	454	448	446	440	437	433	418
	0.8	189	486	494	507	502	500	495	492	489	476
	0.85	200	515	527	546	540	537	531	529	527	519
	0.9	217	558	572	592	590	590	588	586	584	576
	0.925	228	585	602	628	626	625	623	623	622	
	0.95	243	625	645	675	676	677	678	677	676	672
	0.96	251	646	669	704	703	702	701	703	705	
	0.97	263	679	706	746	744	744	742	744	747	
	0.98	283	734	763	806	807	808	809	810	811	815
	0.99	316	820	860	919	925	928	934	936	938	946
	0.999	449	1166	1226	1317	1351	1367	1401	1419	1442	
10 acres	0.1	231	285	271	251	248	247	244	236	226	
	0.2	271	337	322	299	296	295	292	283	271	
	0.3	303	381	363	337	335	333	331	320	306	
	0.4	333	420	402	374		369	366	355	341	
	0.5	361	463	443	413		409	407	394	378	
	0.6	392	508	488	457	<i>4</i> 55	453	451	436	418	
	0.7	426	564	543	511	508	506	503	487	466	
	8.0	469	633	610	576		572	569		529	
	0.85	496	678	655	621	619	618	616	598	575	
	0.9	533	739	717	684		682	681	661	635	
	0.925	557	777	<i>7</i> 57	726		727	727	707	681	
	0.95	588	835	816	788		790	792	769	741	
	0.96	611	875	852	818		819	819	800	777	
	0.97	642	918	900	874		873	872	851	824	
	0.98	681	1003	984	955	955	954	954	926	890	
	0.99	760	1129	1120	1107	1104	1102	1099	1073	1041	
	0.999	1123	1538	1531	1521	1562	1582	1623	1597	1564	1439

	Emission **	30	80	100	130	150	160	180	200	225	320
	Cum. Prob.***			Methyl bror	nide concei	ntration (ug/	m3)				
20 acres	0.1	286	291	281	267	259	255	247	244	241	228
	0.2	336	347	335	317	309	305	297	294	290	275
	0.3	377	392	379	360	350	346	336	333	329	314
	0.4	416	434	420	399	388	383	372	369	366	353
	0.5	450	480	465	442	431	<i>4</i> 26	415	410	404	381
	0.6	489	526	511	489	477	472	460	455	449	<i>4</i> 26
	0.7	529	586	571	548	534	528	514	508	501	474
	8.0	580	659	643	619	604	597	582	576	569	542
	0.85	612	705	689	666	651	644	629	625	619	598
	0.9	657	772	<i>756</i>	733	718	710	695	691	686	667
	0.925	686	813	799	779	766	759	746	740	733	706
	0.95	719	874	863	847	833	825	811	807	802	<i>7</i> 83
	0.96	746	919	902	877	863	855	841	841	841	841
	0.97	780	964	952	935	920	912	897	894	890	875
	0.98	835	1053	1042	1025	1007	998	980	972	963	927
	0.99	927	1182	1186	1191	1167	1155	1131	1128	1125	1112
	0.999	1338	1629	1635	1644	1656	1662	1674	1679	1685	1708
30 acres	0.1	333	297	281	256	253	252	249	248	247	243
	0.2	389	353	334	306	304	302	300	300	300	300
	0.3	437	400	379	347	344	342	339	340	341	345
	0.4	478	444	<b>4</b> 20	385	382	381	378	378	379	381
	0.5	519	490	465	428	424	423	419	419	420	422
	0.6	564	539	513	474	471	469	466	466	465	463
	0.7	608	600	572	530		524	520	520	519	517
	0.8	664	676	646	600		593	589	590	592	598
	0.85	700	723	693	647	645	643	641	641	641	641
	0.9	749	793	761	713		710	708	710	713	
	0.925	781	833	803	758	758	759	759	761	763	
	0.95	821	895	868	827	827	827	827	830	834	849
	0.96	845	945	909	856	857	858	859	866	875	909
	0.97	886	992	960	913		914	915	919	924	943
	0.98	939	1079	1045	994	994	995	995	1001	1008	1035
	0.99	1044	1215	1195	1166	1162	1159	1155	1162	1170	1202
-	0.999	1506	1679	1653	1614	1651	1670	1707	1732	1764	1884

	Emission **	30	80	100	130	150	160	180	200	225	320
	Cum. Prob.***			Methyl bror	nide concer	ntration (ug/	/m3)				
40 acres	0.1	367	304	291	271	265	262	256	256	256	256
	0.2	429	363	347	324	318	314	308	309	311	317
	0.3	482	412	394	367	359	356	348	350	353	364
	0.4	530	457	437	407	400	396	389	391	393	401
	0.5	573	505	<i>4</i> 85	454	445	441	432	<i>4</i> 33	435	441
	0.6	624	555		502	493	489	480	<i>4</i> 81	482	<i>4</i> 86
	0.7	672	617	595	562	552	546	536	537	539	<i>545</i>
	8.0	733	694	671	637	625	619	607	611	615	632
	0.85	772	743	721	687	677	672	662	664	667	678
	0.9	825	815	792	757	747	741	731	735	741	762
	0.925	860	856	836	805	796	792	783	787	793	814
	0.95	906	918	901	875	867	863	855	860	866	889
	0.96	933	970	945	908	900	896	888	897	908	950
	0.97	973	1022	1001	970	960	956	946	953	961	993
	0.98	1035	1107	1086	1054	1044	1039	1029	1037	1046	1082
	0.99	1148	1249	1246	1241	1223	1213	1195	1204	1216	1260
	0.999	1658	1724	1721	1716	1734	1744	1762	1798	1842	2011

<sup>\*</sup> Emission (flux) rate (lbs MB/acre-day) = Maximum application rate (lbs/acre) x emission ratio. MB concentrations (ug/m3) (non-shaded columns) were generated using the air dispersion model, ISCST3, by the use of flux and 5-year weather data from the 4 highest MB use counties (Merced, Ventura, Monterey, and Fresno Counties) (Johnson, 2000a). MB concentrations in the the shaded columns were linear interpolated from simulated MB concentrations (non-shaded areas).

<sup>\*\*</sup> Emission rates (lbs MB/acre-day) in non-shaded columns were used in the simulation; those in the shaded columns were derived to represent flux rates for different soil application methods and maximum application rates as described in 3CCR 6450.3(a).

<sup>\*\*\*</sup> cum. prob. is cumulative probability (e.g. cum. prob. of 0.95 is the 95th percentile).

It is necessary to calculate emission rates, which will be used to determine MB air concentrations from data in Table C.2. Emission rates for MB fumigation are calculated using the following equation:

Emission rate (lbs MB/acre-day) = Emission ratio (ER) x maximum application rate (lbs/acre)

An emission ratio is a fraction of the total applied MB that volatilizes during the 24 hours showing the highest air concentrations. An emission ratio of 0.30 means 30 percent of the total applied MB volatilizes under that specified conditions. Emission ratios of some different soil injection methods are not the same. The emission ratios shown in Table C.3 for different fumigation methods were those recommended by DPR (2001).

The fumigation methods and the maximum application rates are those listed in the current methyl bromide regulations in California Code of Regulations (CCR, 2001). The estimated emission rates for the recommended fumigation methods and the maximum application rates are shown in Table C.3.

Table C.3. Emission rates for different application methods when using maximum application rates.

Maximum MB application rate,		Emission rate
(lbs/acre) (Application method)	Emission ratio	(lbs MB/acre-day)
200 (Nontarp/shallow/bed)	0.4	80
400 (Tarp/deep/broadcast)	0.4	160
400 (Nontarp/deep/broadcast)	0.4	160
250 (Tarp/shallow/bed)	0.8	200
225 (Drip system-hot gas)	1.0	225
400 (Tarp/shallow/broadcast)	0.8	320

The 95<sup>th</sup> percentile MB concentrations (µg/cm² and ppb) at the buffer zone distance were determined from Table C.2 based on these emission rates for field sizes of 1, 10, 20, 30 and 40 acres. These MB concentrations, representing acute exposures, are shown in Tables C.4. The buffer distances for different field sizes and emission rates (DPR 2001) are also shown in Table C.4. The 95<sup>th</sup> percentile MB concentrations should be used in the risk assessment because the exposure at this percentile is generally considered health protective. MB concentrations in Table C.4 are not appropriate for use in the determination of subchronic exposure because exposure days for persons at the buffer zone distance of a particular field will not be lengthy enough to be considered a subchronic exposure. Ambient air concentrations shown in Appendix D (Table D.1) should be considered for a subchronic exposure.

Table C.4. Acute methyl bromide (MB) exposures (95th percentile) of persons at the buffer zone distance following field fumigation.

Field 1 acre			10 acres				20 acres				30 acres				40 acres										
Emission rate*	80	160	200	225	320	80	160	200	225	320	80	160	200	225	320	80	160	200	225	320	80	160	200	225	320
Buffer zone (ft)	110	290	380	420	580	410	1100	1400	1600	2100	610	1600	2000	2300	3100	770	2000	2600	2900	3900	900	2400	3000	3400	4600
MB (ug/m3)	625	677	677	676	672	835	790	769	741	633	874	825	807	802	783	895	827	830	834	849	918	863	860	866	889
MB (ppb)	163	176	176	176	175	217	205	200	193	165	227	215	210	209	204	233	215	216	217	221	239	224	224	225	231

<sup>\*</sup> Notes on emission rates:

1 ppb = 0.26 x ug/m3

The emission rate of 80 lbs MB/acre-day was determined for nontarp/shallow/bed fumigation method.

The emission rate of 160 lbs MB/acre-day was determined for tarp/deep/broadcast fumigation method.

The emission rate of 160 lbs MB/acre-day was determined for nontarp/deep/broadcast fumigation method.

The emission rate of 200 lbs MB/acre-day was determined for tarp/shallow/bed fumigation method.

The emission rate of 225 lbs MB/acre-day was determined for drip system-hot gas fumigation method.

The emission rate of 320 lbs MB/acre-day was determined for tarp/shallow/broadcast fumigation method.

# Appendix D Exposure of Persons to Ambient Methyl Bromide in the High Use Counties

At the request of DPR, ARB conducted MB ambient air monitoring studies in Monterey, Santa Cruz and Kern Counties in 2000. The study periods and sites were selected based upon the historical trends in MB use from 1996 to 1998 (Sanders, 2000). Sanders suggested that monitoring studies should occur over a two-month period during July and August in Kern County, and September and October in Monterey or Santa Cruz County.

# 1. Ambient MB monitoring study in Monterey and Santa Cruz Counties.

ARB conducted MB ambient air monitoring in Monterey and Santa Cruz Counties from September 11, 2000 through November 3, 2000 (ARB, 2001). This monitoring period coincided with the use of MB prior to planting of a variety of crops. The sampling site selection specifically focused on areas of historical use of MB prior to planting strawberries.

Ambient air samples were collected at four sites in Monterey County and one site in Santa Cruz County. At each location, 24-hour samples were collected four days per week for eight weeks. Additional samples were collected for quality control. Air samples for MB (and 1,3-dichloropropene) were collected using evacuated 6 liter Silicosteel® canisters. Each canister sample was analyzed for both compounds. Sampling for MB was also conducted for one week using charcoal tubes. The samplers were placed approximately 5½ feet above the building rooftops for the ambient monitoring. The height of samplers for all sampling sites ranged from 17 to 23 feet above the ground level. The air flow rate for the canisters was 3 standard cubic centimeters per minute (sccpm). MB in canisters was analyzed using gas chromatography equipped with a mass selective detector. MB in charcoal tubes was analyzed using gas chromatography equipped with an electron capture detector.

ARB conducted a field spike recovery study during the sampling period. A small volume (100 mL) of a gas standard, with a certified concentration of MB, was added to an evacuated canister. The field spikes were collected by sampling ambient air into the previously spiked canisters and were collocated with an ambient sample (same location, flow rate and sampling time). The collocated (unspiked) sample result is subtracted from the field spike sample result before calculation of percent recovery of the analysis. A similar field spike recovery study was also conducted for charcoal tubes. A small volume (20  $\mu$ L) of a solvent standard with a known amount of MB was added to the charcoal cartridges. The average recoveries for MB field spikes were 58% for charcoal tubes and -5% for canisters. The negative recovery for canisters resulted because the ambient air concentration of MB was much higher than the spiked amount. The average MB recoveries for laboratory and trip spikes were 101 and 101%, respectively.

# 2. Ambient MB monitoring study in Kern County.

ARB conducted an ambient air monitoring study in Kern County from July 19, 2000 through September 1, 2000 (ARB, 2000). This study period coincided with the use of MB prior to planting of a variety of crops. The sampling site selection specifically focused on the use of 1,3-dichloropropene prior to planting carrots. In one case, Cotton Research Station (CRS) was selected for monitoring based on its proximity to the use of MB on roses. The sample collection

method, MB analysis and field spike were similar to those employed in the study in Monterey and Santa Cruz Counties. At each location, 24-hour samples were collected four days per week for seven weeks. Additional samples were collected for quality control. The average field spike recovery of MB using canisters was 102%. A field spike recovery of MB was not performed for charcoal tubes.

# 3. Calculations of MB air concentrations.

Powell (2001) summarized air concentrations of MB obtained from the studies in Monterey, Santa Cruz and Kern Counties. MB in charcoal tubes for Monterey and Santa Cruz Counties were not used because the identities of some of collected samples were lost (mislabeled). Only thirteen samples from six sites were analyzed and the results were indicated "nondetectable." The MB air concentrations from the canisters are grouped into 24-hour (daily), 7-day (weekly) and 7 or 8-week concentrations (Table D.1). MB concentrations from the studies were not adjusted for field spike recoveries because the average recovery was approximately 100%. Powell (2001) indicated that before calculating the exposures, one-half the detection limit was substituted for two Kern County samples that were below the detection limit. (No samples in Monterey/Santa Cruz were below the quantitation limit.). The detection limit for methyl bromide was 7.1 ng/m<sup>3</sup> (0.00182 ppb). Further, where there were pairs of collocated samples for the same day, the two values were averaged. The 95<sup>th</sup> percentile values were calculated using the following equations:

# 24-hour exposure:

95<sup>th</sup> %ile = exp{arithmetic mean of log concentrations +  $t_{(.95; n-1)}$  x (standard deviation of logs)}

# 7-day exposure:

95<sup>th</sup> %ile = arithmetic mean of week means +  $t_{(.95; n-1)}$  x (standard deviation of week means).

# 7- or 8-week exposure:

For each monitoring site separately, 7- or 8-week exposure is the mean concentration over the monitoring period. It is calculated as the arithmetic mean of the 8 (7 in Kern County) weekly means calculated as above for 7-day exposure.

It is important to note that these ambient air concentrations were obtained from sampling stations that were not necessarily located at the buffer zone distance like those derived from the model shown in Section 4 of Appendix C (Exposure of residents to MB from living at the buffer zone distance). The daily MB exposure obtained from the model and that from the ambient monitoring studies may be used in risk assessment under different exposure scenarios. Persons (such as residents, school children, and bystanders) would be more likely to be exposed to ambient MB than they would be exposed to MB at the buffer zone distance. Ambient MB from the studies represents a realistic exposure scenario during the peak use period, whereas the latter was obtained from the model, which may not represent a realistic exposure situation.

Table D.1. Methyl bromide concentrations (ppb) based on the Air Resources Board 2000 monitoring studies in Monterey, Santa Cruz and Kern Counties.<sup>a</sup>

		I	Daily	We	ekly	7 or 8-week							
	Monitoring	Maximum	95 <sup>th</sup> percentile	Maximum	95 <sup>th</sup> percentile	Mean of							
Site <sup>b</sup>	days 24-hour 24-hour			weekly mean		weekly means							
Moi	nterey and San	ta Cruz Coun	ties (8 monitoring	ring weeks, September 11 – November 3, 2000)									
	ppb												
CHU	31	2.41	2.26	1.61	1.63	0.644							
LJE	30	24.0	18.5	10.5	11.1	3.79							
OAS	31	1.84	1.21	1.01	0.918	0.387							
PMS	31	30.8	30.2	15.5	17.1	7.68							
SAL	31	7.91	6.17	3.01	3.14	1.29							
SES	31	16.4	12.2	8.30	7.45	2.60							
		Kern Count	y (7 monitoring w	eeks, July 19 – S	September 1, 200	0)							
				ppb									
ARB	25	0.996	0.556	0.507	0.507	0.189							
CRS	24	14.2	25.4	4.59	5.54	2.16							
MET	26	0.224	0.239	0.145	0.163	0.084							
MVS	26	0.487	0.262	0.201	0.195	0.092							
SHA	26	3.52	3.98	1.77	2.05	0.792							
VSD	26	0.347	0.292	0.175	0.181	0.099							

<sup>&</sup>lt;sup>a</sup> Methods and equations used to derive different categories of air concentrations are shown in Appendix D, section 3 - Calculations of MB air concentrations.

Names of ambient sampling sites (Monterey and Santa Cruz): Chualar School (CHU), La Jolla Elementary School (LJE), Oak Avenue School (OAS), Pajaro Middle School (PMS), MBUAPCD Ambient Monitoring Station, Salinas (SAL), Salsepuedes Elementary School (SES); (Kern): ARB Ambient Monitoring Station (ARB), Cotton Research Station (CRS), Mettler-Fire Station (MET), Mountain View School (MVS), Shafter-Walker Ambient Monitoring Station (SHA), Vineland School District-Sunset School (VSD).

# Appendix E Adjusted Acute and Nonacute Exposure Estimates of Persons in California to Methyl Bromide

Previously, acute and nonacute (subacute, subchronic, and chronic) MB exposures (Table 11) were calculated for persons during soil, commodity, and structural (brewery facility) fumigations by using work hours obtained from a survey (Appendix A). Current MB regulations for soil fumigation or permit conditions for greenhouse, potting soil, and commodity fumigations specify daily work hours for persons, who may be exposed to MB. Consequently, the exposure estimates were recalculated based upon work hours indicated in the regulations or permit conditions. The recalculation did not include exposures of residents to MB during commodity fumigation, from living at the buffer zone distance, or to ambient MB in the high use counties because the MB concentration used in the calculation was either a default value, determined from a mathematical model or obtained from sampling of ambient air.

In cases where the same study shows exposure for growers and PCOs (Table 11), only the exposure for PCOs is used in Appendix E. Basically, adjusted average acute exposures for growers and PCOs are the same because the current regulations and permit conditions do not separate work hours for growers and PCOs. However, if a study shows exposure for growers only, the exposure is used in Appendix E.

Nonacute exposures are normalized (amortized) by employing adjusted acute exposure estimates and workdays (exposure days) for each of these three groups of exposure. Adjusted exposures are calculated as follows:

Adjusted average acute exposure =  $\underline{\text{Average acute exposure (Table 11) x work hours (allowed)}}$ work hours (previously used)

Adjusted average subchronic exposure =  $\underline{\text{Adjusted average acute exposure x workdays in 90 days}}$ 90 days

Adjusted average chronic exposure = <u>Adjusted average acute exposure x workdays per year</u> 365 days

The upper bound exposure estimate for the adjusted average acute exposure was also calculated by using the following equation:

Adjusted upper bound acute exposure = (Adjusted average acute exposure + (1.645 x Adjusted standard deviation for acute exposure))

Adjusted acute and nonacute exposure, and upper bound acute exposure estimates are shown in Appendix E.

Appendix E
Adjusted Acute and Nonacute Exposure Estimates of Persons in California to Methyl Bromide(a)

		Acute	e exposure	(ppb)(b)		Subacu	te exp. (ppb)	Subchron	ic exp. (ppb)		
Number/				Adjusted a	0 (		ay period		ay period		lay period
Type of application (Data from Table)	Avg.	Used	Allowed	Avg.	Upper	Days	Adj. Avg.(e)	Days	Adj. avg.(f)	Days	Adj. avg.(g)
a) Shallow shank-tarped soil injection fumigation (Table B.1 Applicators: Noble plow shanks	111	5.8	4	77	188	6	66	40	34	n/a	n/a
a) Shallow shank-tarped soil injection fumigation (Table B.2 Co-pilots: Noble plow shanks	) 224	5.8	3	116	245	6	99	40	51	n/a	n/a
a) Shallow shank-tarped soil injection fumigation (Table B.3 Shovelmen: Noble plow shanks	) 147	5.8	3	76	191	3	33	n/a	n/a	n/a	n/a
a) Shallow shank-tarped soil injection fumigation Tarp removers (Table B.4)(h)	835	6	7	974	2118	5	696	55	595	n/a	n/a
b) Nontarp deep shank injection fumigation (Table B.6) Applicators Co-pilots Cultipacker	154 49 99	5.8 5.8 5.8	4 4 4	106 34 68	281 89 181	6 6 6	91 29 59	40 40 n/a	47 15 n/a	n/a n/a n/a	n/a n/a n/a
b) Nontarp deep shank injection fumigation (improved) (Tab Applicator Cultipacker	le B.6) 57 70	5.8 5.8	4 4	39 48	104 128	6 6	34 41	40 n/a	17 n/a	n/a n/a	n/a n/a
c) Nontarp deep shank injection fumigation (Table B.7) Applicator: Basic + a second tractor with a disc Disc driver: Basic + a second tractor with a disc Applicator: Basic + a cultipacker Supervisor: Basic + a cultipacker Cultipacker: Basic + a cultipacker	88 512 94 67 34	5.8 5.8 5.8 5.8 5.8	4 4 4 4	61 353 65 46 23	171	6 6 6 6	52 303 56 40 20	40 40 40 40 n/a	27 157 29 21 n/a	n/a n/a n/a n/a n/a	n/a n/a n/a n/a n/a
d) Nontarp deep shank injection fumigation (Table B.8) Applicator: With 4 forward curved shanks Cultipacker: 4 forward curved shanks	7 7	5.8 5.8	4	5 5	13 13	6 6	4	40 n/a	2 n/a	n/a n/a	n/a n/a

- (a) MB exposure estimates shown in Table 11 were adjusted for work hours allowed by current regulations or permit conditions for acute exposures.
- (b) acute exposure is the exposure is 30 days or longer in a 90-day period; chronic exposure is the exposure where days of exposure is 120 days or longer in a 365-day period.
- (c) hour (used): Previously used in the calculation of exposure estimates; hour (allowed): based on the current MB regulations or permit conditions.
- (d) adjusted upper bound MB concentrations = (average+(1.645 x STDEV)) x hours allowed/hours used. When there is one or two data points, the STDEV is assumed to be equaled to that data point or the average of two data points.
- (e) average subacute exposure = average acute exposure x workday per week/7 days.
- (f) average subchronic exposure = average acute exposure x workdays in 90 days/90 days.
- (g) average chronic exposure = average acute exposure x workdays in 365 days/365 days.
- (h) tarp removers removed tarp the same day the tarp was cut. This tarp cutting practice was not in compliance with the current regulations.
- (i) MB concentrations in work areas must be monitored and the work hours adjusted accordingly so that the daily exposure will not exceed the target level. The maximum exposure estimate is assumed to be 210 ppb. MB concentration of 210 ppb was used to calculate subacute, subchronic and chronic exposures when estimated MB air concentration is greater than 210 ppb. Otherwise, the average acute exposure was used for the calculation.

  Abbreviations: exp. is exposure; PCO is pest control operator; Avg. is average; inj. = injection; n/a = not applicable.

Appendix E (continued 1)
Adjusted Acute and Nonacute Exposure Estimates of Persons in California to Methyl Bromide(a)

			exposure							Chronic exp. (ppb)	
Number/	A			Adjusted a			ay period		y period		ay period
Type of application (Data from Table) e) Shallow shank-tarped bed fumigation (Table B.9)	Avg.	Usea	Allowed	Avg.	Upper	Days	Adj. Avg.(e)	Days	Adj. avg.(f)	Days A	Adj. avg.(g)
Applicator: Conventional+raised platform&inj. 8" Co-pilots: Conventional+raised platform&inj. 8"	80 104	5.8 5.8	4 4	55 72	146 190	6 6	47 61	40 40	25 32	n/a n/a	n/a n/a
Applicators: Conventional+closing shoes Co-pilots: Conventional+closing shoes	44 167	5.8 5.8	4	30 115	80 305	6 6	26 99	40 40	13 51	n/a n/a	n/a n/a
f). Shallow shank-tarped bed fumigation (Table B.10) Driver: Tractor was equipped for fumigation Applicator: Tractor was equipped for fumigation Tape layer: Tractor was equipped for fumigation	28 45 65	5.8 5.8 5.8	4 4 4	19 31 45	51 82 119	6 6 3	17 27 19	40 40 n/a	9 14 n/a	n/a n/a n/a	n/a n/a n/a
Driver: Tractor was equipped for laying tarp Co-pilot: Tractor was equipped for laying tarp	4 34	5.8 5.8	4	3 23	7 62	6 6	2 20	40 40	1 10	n/a n/a	n/a n/a
g). Shallow shank, tarped-bed fumigation (Table B.11) Applicator Co-pilot Shovelman	2 32 0.6	5.8 5.8 5.8	4 4 4	1 22 0.4	4 58 1	6 6 3	1 19 0.2	40 40 n/a	1 10 n/a	n/a n/a n/a	n/a n/a n/a
h). Tarp shallow with Noble plow shanks (Table B.12) Cutter: From broadcast application Puller: From broadcast application	82 33	6 6	4 7	55 39	202 215	5 5	39 28	30 30	18 13	n/a n/a	n/a n/a
i). Tarp shallow with Noble plow shanks (Table B.13) From use of high barrier (HB) tarp Cutter Remover: Tractor driver Remover: Basketman Remover: End puller	78 343 325 7	6 6 6	4 7 7 7	52 400 379 8	138 1058 1003 22	5 5 5 5	37 286 271 6	30 30 30 30 30	17 133 126 3	n/a n/a n/a n/a	n/a n/a n/a n/a
2.a. Worker exposure assessment during potting soil fumigate 2.b. Greenhouse soil fumigation (Table B.14)  Tarp venters(i)  Tarp removers(i)	0.009 0.95	sable data 1 1	a) varied varied	0.01 0.95	210 210	1 1	0.001 0.14	n/a n/a	n/a n/a	n/a n/a	n/a n/a
3. Fumigation of grain products (chambers, sea containers) (The initiation of aeration of sea containers/truck trailers  Aerator(i)		6	varied	0.6	210	5	0.43	45	0.30	180	0.30
Initiation of aeration of tarpaulin fumigation Aerator(i) Emptying sea containers/truck trailers	0.025	6	varied	0.03		5	0.02	45	0.01	180	0.01
Forklift driver(i) Emptying non-certifying fumigation chambers Forklift driver(i)	16 6	1 1	varied varied	16 6		5 5	11 4	45 45	8	180 180	8

Appendix E (continued 2)
Adjusted Acute and Nonacute Exposure Estimates of Persons in California to Methyl Bromide(a)

			e exposure							Chronic exp. (ppb)	
Number/				Adjusted a			ay period		y period		lay period
Type of application (Data from Table)	Avg.	Used	Allowed	Avg.	Upper	Days	Adj. Avg.(e)	Days	Adj. avg.(f)	Days .	Adj. avg.(g)
4. Fumigation of dried fruit and tree nut products (Table B.16)	6)(h)										
Chamber (raisins):											
Fumigators(i)	63	1.5			210		54	63	44	150	26
Aerators(i)	47	1.5			210		40	63	33	150	19
Clear chambers 1-2(i)	1434	1.5		210			180	63	147	150	86
Stem pickers(i)	28	8	varied		210		24	63	20	150	12
Forklift driver(i)	3	1	varied	3	210	6	3	63	2	150	1
Hopper operator(i)	19	8	varied	19	210	6	16	63	13	150	8
Area sampling:											
Fumigation chambers(i)	88	1.5	varied	88	210	6	75	63	62	150	36
Fumigation cage(i)	54	1.5		54	210		46	63	38	150	22
Leak checkers-chambers 4-5(i)	4	0.5		4	210		n/a	n/a	n/a	n/a	n/a
Aeration-chambers 4-5(i)	116	1.5		- 1			99	63	81	150	48
Clearing-chambers 4-5(i)	46	1.5			210		39	63	32	150	10
Hopper areas(i)	8	8		8	210		7	63	6	150	19
	27	0		27	210		23	63	19	150	11
Stem picker(i)	21	٥	varied	21	210	0	23	03	19	130	11
<ul><li>5. Measurement of MB exposure to the fumigators, forklift d</li><li>6. Methyl bromide air monitoring studies at a walnut process</li><li>a) Worker exposure studies:</li></ul>				er workers (	no usable	e data)					
	2.4	0		2.4	210	_	20	75	20	/	/
Bulk packaging(i)	34 208	8 8		34 208	210 210		29 178	75 75	28 173	n/a n/a	n/a n/a
Cleaning plant(i)	208 87	5.5			210		75	75 75		n/a 180	
Fumigatorium(i)									73		43
Packaging(i)	44	8	varied	44	210		38	75	37	n/a	n/a
Vacuum chamber(i)	239	8	varied	210			180	75	175	n/a	n/a
Sorting(i)	32	8		32	210		27	75	27	n/a	n/a
Special cracking(i)	29	8	varied	29	210	6	25	75	24	n/a	n/a
b) Area samples:											
Sorting line(i)	83	8	varied	83	210	2	24	n/a	n/a	n/a	n/a
d) Compliance monitoring:											
Sorting line in cleaning plant(i)	318	8 8	varied	210			180	75	175	n/a	n/a
Cello packaging of in-shell walnuts in main bldg.(i)	355	8	varied	210			180	75	175	n/a	n/a
Bulk packaging of in-shell walnuts in main bldg.(i)	243	8	varied	210	210	6	180	75	175	n/a	n/a
7. Fumigation and aeration at a brewery facility (Table B.18) a) Applicators											
Entry and reentry to open canisters/cylinders(i)	28.9	1.1	varied		210		8	n/a	n/a	n/a	n/a
Area sample (door to buffer zone)(i)	42	8	varied	42	210	2	12	n/a	n/a	n/a	n/a
b) Aerators											
Aerators(i)	25	0.6	varied	25	210	2	7	n/a	n/a	n/a	n/a
Area sample (left of entrance door)(i)	173	8		173	210		49	n/a	n/a	n/a	n/a
Area sample (on applicator's truck)(i)	100	8		100			29	n/a	n/a	n/a	n/a
bumple (on applicator 5 track)(1)	100	U	, arroa	100	210		2)	11, 4	11/α	11, 4	11/ U